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KAMINISTIKWIA RIVER: ACUTE LETHALITY AND CHLOROPHENOL BIOCONCENTRATION IN FISH EXPOSED DOWNSTREAM OF A COMBINATION GROUNDWOOD SULFITE AND BLEACHED KRAFT MILL EFFLUENT

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Jim Bradley
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KAMINISTIKWIA RIVER: ACUTE LETHALITY AND CHLOROPHENOL BIOCONCENTRATION IN FISH EXPOSED DOWNSTREAM OF A COMBINATION GROUNDWOOD, SULFITE AND BLEACHED KRAFT MILL EFFLUENT

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ADDENDUM

The company in this study, Great Lakes Forest Products (GLFP), is now called Canadian Pacific Forest Products (Thunder Bay Division), but for purposes of this report will be referred to by its name at the time of the study.

SUMMARY

The Bioassessment Unit, Water Resources Branch and the Ministry's Northwestern Region undertook two fish bioassay assessments in the Kaministikwia (Kaministiquia) River downstream of Great Lakes Forest Products. These studies were carried out in August 1985 and 1986, as part of the MISA pilot site project on the lower Kaministikwia River, to assess the effects of a large pulp and paper mill complex on water quality in a riverine setting. They were also undertaken to provide an update on potential effects of the mill on the Kaministikwia River fishery, for the Region to use in future control order negotiations with Great Lakes Forest Products. For the purpose of the control order process, the tabulated results and major conclusions from this study were made available to the region in December, 1986. A dissolved oxygen survey was also undertaken by the region in 1987 and some of those findings are included in this report.

During the study, fish were exposed in cages at various sites in the river to measure acute lethality downstream of the mill. Chemistry analyses of the river and mill effluents for contaminants and laboratory bioassays of the effluent were undertaken in support of the field study. Upon completion of the work, fish surviving the field exposure were sacrificed and analyzed for chlorophenols.

Laboratory bioassays of the Great Lakes Forest Products Diffuser effluent demonstrated that the mill did not meet the fish survival requirement of the Ontario Government. The lethality observed in the bioassays was due to unidentified toxicants in the pulp and paper mill wastes.

The Great Lakes Forest Products Diffuser effluent produced mortality in caged fish in two main sections of the river downstream of the mill. Those sections of river extended from 30 m downstream of the Diffuser to the inflow to the Westfort Turning Basin and from the Hwy 61B swing bridge downstream into the Mission River, to at least as far as the Hydro property. These findings are consistent with fish kill

observations in the Kaministikwia River at various times since 1966, and are due to the Great Lakes Forest Products effluent, in combination with low flow conditions in the river. The primary cause of the acute lethality downstream of the mill is depressed dissolved oxygen levels in the river. Furthermore, there is no reason to believe that the situation has changed up until now, the spring of 1989, for no additional treatment systems have been added to the mill since this study was undertaken. The bioconcentration of chlorophenols by caged fish occurred in the river downstream of the Great Lakes Forest Products mill, at levels similar to those found in young-of-the year walleye taken from the river during the 1986 study. However, based on those levels in fish and sublethal studies in the literature, it is concluded that chlorophenol bioconcentration in the Kam River biota would not likely cause a detrimental effect on the fishery.

INTRODUCTION

I. Study Objectives

This report presents an assessment of the acute effects of the Great Lakes Forest Products (GLFP) mill effluent on caged fish in the Kaministikwia (Kam) and Mission Rivers. The study was undertaken in August, 1985 and repeated in August, 1986 as a joint venture of the Industrial Abatement Section and Water Resources Assessment Unit, of the Ministry's Northwestern Region, and the Bioassessment Unit of the Water Resources Branch, with support from Lakehead University. The objectives of the study were:

1. to determine the extent of fish lethality within the Kam and Mission Rivers downstream of Great Lakes Forest Products, under low flow conditions in the river (17 m^3/s - 1986).

2. to determine the cause/effect relationship between the effluent plume characteristics and field bioassay results, with special emphasis on dissolved oxygen levels and related effects.

3. to measure chlorophenol levels in the river downstream of the pulp mill and related chlorophenol bioconcentration by fish exposed *in situ*.

II. Study Area

The Kam River originates approximately 40 km northwest of Thunder Bay, as two Ontario Hydro controlled discharges, one each from Shebandowan and Dog Lakes. The upper reaches of the river consist of a series of falls and rapids while the lower river, the subject of this study is fairly sluggish. Peak flows during storm events in the summer reach 50 or 60 m^3/s, while under low flow conditions, a flow of at least 17 m^3/s is maintained by Ontario Hydro at its Kakabeka Falls Dam. The average flow over the 5 days of this study was

18.5 m³/s. There are no major pollution sources upstream of Great Lakes Forest Products and in the last 8 km, the river passes through the city of Thunder Bay and discharges into Lake Superior through three channels. The first channel, known as the Mission River, is approximately 3 km long and carries 40-50% of the Kam River flow to the lake. (Figure 1).

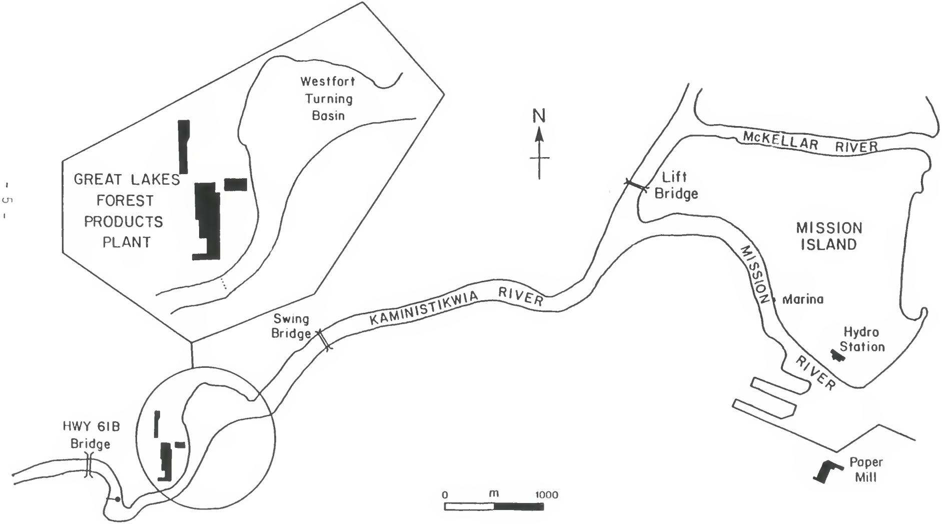
Our study was confined to the Kam River from just north of the Hwy. 61A bridge down and into the Mission River as far as the Ontario Hydro property. Reichhold Chemicals was the only industrial input in the study area downstream of GLFP. However, its' effluent input in terms of flow to the river (.004 m³/sec) was insignificant when compared to the 2.95 m³/sec flow from GLFP (Klose, 1988). As a matter of record, Reichhold Chemicals now dischargers its treated effluent to the city's sanitary sewer (as of January, 1988).

The Thunder Bay Salmon Association's Hatchery was constructed on the Kam River in September, 1987 in order to supply a "put and take" fishery in the Thunder Bay Harbour/Kam River area. The lower Kam River is required as a pre-smolt nursery area, prior to the young salmon migration into Lake Superior. A zone of passage past the GLFP plant discharges is also required for spawning runs by the adult fish returning from the lake.

III. Mill Description

Great Lakes Forest Products Ltd. is located on the north shore of the Kam River, in Thunder Bay, 9 km upstream of Lake Superior. The mill originated in 1924 as a groundwood facility and a sulfite mill was added in 1926. Two newsprint machines started up in 1929, with two more machines following in 1958. The bleached kraft mill facilities became the last two major expansion projects, one (the A mill) in 1966 and the other (the B mill) in 1976. The latter BKM employed the Reeve-Rapson "closed cycle concept" of operation to minimize water use and contaminant discharges. However, that process had to be abandoned after several years of operation (Bonsor et al., 1988).

FIGURE 1: STUDY AREA.



The current facility is a combination groundwood, sulfite and bleached Kraft pulping operation. The mill produces approximately 1100 tonnes of newsprint and 1000 tonnes of bleached kraft pulp per day using mainly a softwood mix (black spruce, jack pine, balsam fir, etc.) and some poplar in the kraft, groundwood and sulfite pulping processes. Effluent treatment includes several clarifiers in the newsprint mill, pH adjustment of the kraft mill effluents, bisulfite liquor recovery, a steam stripper and a closed cycle process in the "B" kraft mill. There was no secondary treatment facility employed by the company at the time of this study and no new effluent treatment systems have been added up until the spring of 1989 (Murphy, pers. comm.). The process effluent is discharged to the river adjacent to the mill through a submerged diffuser, while the cooling water is discharged to the Westfort turning basin by way of a submerged discharge at the river shoreline (the "Clean" Water discharge).

IV. Background

Biochemical Oxygen Demand (BOD) is an important indirect measure of the oxygen-consuming properties of liquid industrial wastes. GLFP discharged an average BOD of 43 tonnes/day in 1986, which is 'the most massive discharge of BOD among nine bleached kraft mills in Ontario' (Bonsor et al, 1988). GLFP was the major source of BOD loadings to the Kam River with 46.8 tonnes/day discharged during this study (Klose, 1988). That level was 4500 times greater than loadings discharged by the only other BOD source (Reichhold Chemical), located on that part of the river studied in this report (Klose, 1988).

Fish kills have been reported in the Kam River since 1966. The kills which occurred in 1969 and 1970 were due to low river flows and low dissolved oxygen levels (D.O.), high temperatures and in the case of the 1969 event, an accidental spill of kraft mill wastes (Beak, 1986).

The largest known kill occurred in 1977. Low flows and low oxygen levels occurred coincidentally with the longnose sucker spawning run, causing a massive kill of 10,000 fish (Beak, 1986). Between May 26th and August 24th of that year, 8 of 10 measurements at the Hwy. 61B swing bridge had dissolved oxygen levels of less than 4.0 mg/L, while 5 of those measurements were less than 3.0 mg/L (OME, 1978a). The lowest levels found in 1977 occurred at the Mission River junction, where 6 of 7 measurements from May 26 to August 8th were between 0.2 and 1.8 mg D.O./L (OME, 1978a).

The next major prolonged period of low oxygen levels occurred in 1980. At the Hwy. 61B swing bridge, 6 of 18 samples had D.O. levels below 2 mg/L, 12 of 18 were below 3.0 mg/L, 13 of 18 were below 4.0 mg/L and 17 ~~and~~ of 19 were below 5.0 mg/L, during the period from May 28th to September 12, 1980. A fish kill observed by Ontario Hydro personnel occurred in the Mission River in 1980. (Beak, 1986). Dissolved oxygen levels in the river near that site ranged from 0 - 1.4 mg/L, in 4 samples measured between May 6th and August 26th. The current Water Quality Objectives of the Ontario Ministry of the Environment (OME) states that: "At no time should dissolved oxygen concentrations be less than .... 5 mg/L for cold water biota .... and ... 4 mg/L for warm water biota", when ' water temperatures are 20°C' (OME, 1978b).

The salmon hatchery on the Kam River upstream of Great Lakes Forest Products began operating in October, 1987. A fish survey undertaken as part of the Thunder Bay Remedial Action Plan found that the Kam River downstream of the plant had good potential as a larval fish habitat (Momot, unpub. report). However, to avoid possible dissolved oxygen problems in the river, the hatchery stock may have to be released directly into Thunder Bay harbour.

METHODS

I. Study Outline

In August of 1985, hatchery-reared smallmouth bass and lab-reared fathead minnows were exposed in cages at various sites in the Kam River, to measure acute lethality downstream of Great Lakes Forest Products. A storm event at the initiation of the study negated attempts to have the exposure performed under low flow conditions. Hence, a second exposure with hatchery-reared brown trout and lab-reared fathead minnows was undertaken in both the Kam and Mission Rivers, under low flow conditions in August 1986. Daily observations of fish mortality and water chemistry sampling were undertaken at each exposure site for both studies.

During the in situ exposures, daily 24-h composite samples of the diffuser effluent were collected for lab bioassays using rainbow trout. Samples of the effluents were also submitted to the OME Rexdale lab for chemical analyses.

Upon completion of the study, fish surviving the in situ exposure were sacrificed and preserved for chlorophenol analyses.

II. Field Exposure

1. Test Fish

(a) The 1985 Fish Stocks

The fathead minnow (Pimephales promelas) stock of 30-40 days in age were obtained from the USEPA lab in Duluth, Minnesota on May 29, 1985. A portion of the stock was used for the 1985 study and the rest were set aside and became the parental stock for the 1986 fish requirements. The fish to be used in the 1985 study were held in the OME Rexdale lab at 25-26°C and fed a frozen brine shrimp diet supplimented with Tetra Min^{TM} tropical fish food for 1½ months. On the last six days at the lab, the fish holding temperature was reduced 1°C/day to 20°C.

The fish were then shipped to Lakehead University in Thunder Bay for a 12-day acclimation period under soft water (approximately 50 mg/L hardness as $CaCO_3$) conditions and a water temperature of 20°C, prior to testing. At the time of testing, the fish were approximately 4-months old and sexually immature.

The smallmouth bass (Micropterus dolomieu) were obtained from the MNR's Sandfield Fish Hatchery on Manitoulin Island and shipped air express to Thunder Bay via Sudbury. The 10-day acclimation period in Thunder Bay involved conditions identical to those for the fathead minnows, with the exception that the bass were fed a trout chow diet similar to that received at the Sandfield hatchery.

(b) The 1986 Fish Stocks

Fathead minnows (Pimephales promelas) were hatched and reared at the MOE Rexdale lab under conditions similar to those used in 1985. They were shipped to Lakehead University and acclimated at 19°C for 26 days prior to testing.

The brown trout (Salmo trutta) were obtained from the MNR Codrington hatchery and shipped immediately to Lakehead University to be acclimated in a manner similar to the 1986 fathead minnows, for a period of 24 days prior to testing.

2. Fish Cages

The cages used in this study were constructed with a 1.9 cm (¾") polyvinylchloride (PVC) pipe frame with a triangular shape, top and bottom, and had three sides, each 0.5 m in length and depth. The frame supported a 0.6 cm (¼") mesh nylon bag with a draw string closure at the top.

The cages were free-floating with the cage top at the water surface and were held in place by a rope and anchor. An empty plastic container was tied to the cages as a navigational marker.

3. Cage Locations

Cage sites near the mill were selected in order to evaluate water quality at the water intake and at each of the discharges (Figure 2, blown-up portion). Other cages were positioned at strategic or well-marked locations such as the inflow and outflow from the Westfort turning basin, the Hwy. 61B swing bridge, etc. Attempts were made to locate the cages used in 1986 at the same locations as used in 1985. Two new locations (sites 10 and 11) were added in 1986, both of which were located in the Mission River. (Figure 2).

4. Procedure

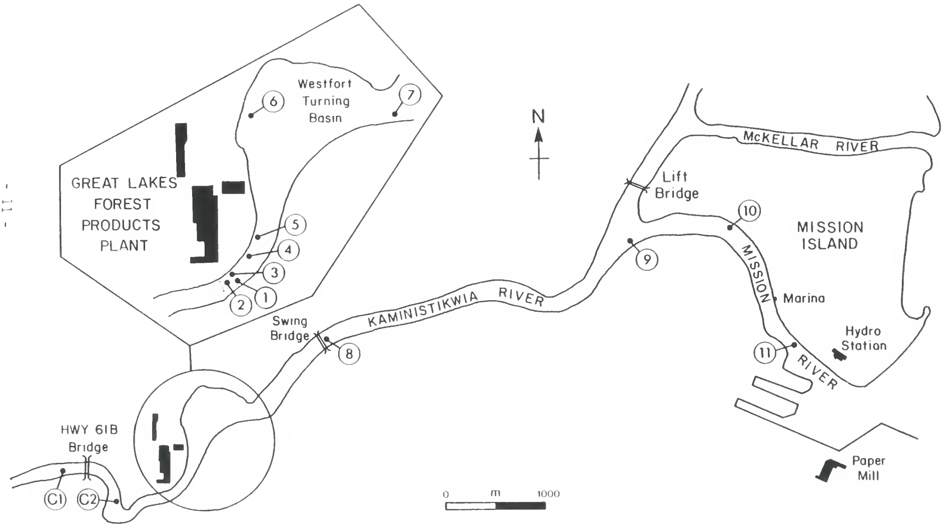
The cages were sited in pre-selected locations on the day before each of the (1985 and 1986) studies commenced. On the following day (August 12, 1985 and August 11, 1986), the fish were placed in the appropriate cages, with the number of fish per cage dependent on the size of the test fish and the amount of biomass needed for contaminant analyses.

In 1985, 50 fathead minnows or smallmouth bass were placed in separate cages with fathead minnows exposed at all sites and smallmouth bass exposures limited to sites C-1, 2, 4 and 6.

In 1986, 25 brown trout or 40 fathead minnows were placed in separate cages with the trout exposed at all sites and fathead minnows exposed at sites C-1, 2, 4, 6 and 11 only, due to the limited number of test fish available.

Mortality checks were undertaken once daily over a 96-h exposure unless the fish were found to be under stress during the initial daily observations. In certain situations in the

FIGURE 2: FISH EXPOSURE SITES IN THE KAMINISTIKWIA AND MISSION RIVERS.



1986 study, dead fish at some sites were discovered shortly after death (i.e. fish still had good body and eye colour) and hence fish from those sites (trout at sites 2, 10 and 11) were preserved and submitted for analyses. Otherwise, dead fish were removed immediately upon observation and discarded. After the 96-h exposures in 1985 and 1986, 3-5 sets of composite samples each containing 5 fish or more were selected from individual sites for analysis of chlorophenols. These fish were batched according to species, sacrificed, weighed as composites, wrapped in hexane-washed foil and frozen for preservation. A pre-exposure set of fish composites was also set aside at the Thunder Bay lab for chlorophenol analyses.

The study dates and corresponding time descriptions at the beginning and end of the study are as follows:

1985 Date	Time	Study Day	Exposure Time
August 12	1200-h	1	0 hours
August 16	1200-h	5	96 hours
1986 Date			
August 11	1200-h	1	0 hours
August 15	1200-h	5	96 hours

III. Physical and Chemical Analyses

1. List of Analyses

i) total reactive phenolics
ii) chlorophenols
iii) phenoxy acids (1986 only)
iv) resin and fatty acids
v) organosulfur compounds
vi) miscellaneous compounds - Na, NH_4-N, NO_3-N (1985 only)
vii) metals scan - Al, Cr, Cu, Zn, Hg, Fe, Pb, Cd (1985 only)
viii) dissolved oxygen, conductivity, pH and temperature

2. Water Sampling Schedule

(a) Effluent Samples

Dissolved oxygen and temperature measurements were not performed on any of the effluent samples. All other analyses in 1985 or 1986, as listed above, were undertaken on 24-h composite samples from the GLFP effluent diffuser or clean water discharge, with two exceptions. The chlorophenol and phenoxy acid samples were collected daily, but as grab samples only.

(b) River Water Samples (at the cage sites)

All field collections were grab samples taken from 0.5m below the river surface.

i) total reactive phenolics - 1985/86 - sampled daily all sites

ii) chlorophenols - 1985 - sampled on days 1, 3 and 5 at all sites
  - 1986 - sampled daily at all sites

iii) phenoxy acids - 1986 - sampled daily at all sites

iv) resin and fatty acids - 1985 - sampled on study days 1 and 2 at all sites, and thereafter sampled only from cage sites at which significant fish mortality occurred
  - 1986 - sampled on study days 1, 2, and 3; otherwise, same as in 1985

v) organosulfur compounds - 1985 - sampled at sites 1-6 only on study day 3
  - 1986 - sampled at sites 1-3 only on study days 1, 2 and 3

vi)	sodium, ammonium and nitrates	- 1985 only - daily at all sites
vii)	metals scan	- 1985 only - daily at all sites
viii)	dissolved oxygen, temperature and conductivity	- 1985 - once daily at all sites - 1986 - once daily at all sites unless significant mortality occurred. In these cases, dissolved oxygen done as often as possible on any given day
ix)	pH	- 1985 - once daily on study days 1-4 - 1986 - once daily on study days 1-5

The analytical methods for these parameters are described in the OME (1983) document entitled "Handbook of Analytical Methods for Environmental Samples."

(c) Bioassay Samples

Daily 24-h composite samples of the Diffuser (alias "Combined") effluent were collected during the 1985 and 1986 studies on all study days except one. On August 12,1985, a grab sample of the Diffuser effluent was collected for testing.

A Clean Water (cooling water) grab sample was also collected on August 12, 1985 in order to bioassay the "Total Mill Effluent" (TME). The TME is a composite of both the Diffuser and Clean Water outfalls, combined in proportion, relative to their flows. Another TME sample was tested in 1985, using 24-h composite samples from each of the two outfalls, on the forth day of the study (August 16, 1985). Likewise, a sample of TME from the first day of the 1986 was tested, and it involved 24-h composite collections.

A sample of the Clean Water Discharge was tested once in 1985 and twice in 1986.

IV. Laboratory Bioassay

The bioassays were 96-h aerated static tests using rainbow trout to measure acute lethality and were carried out in accordance with the procedures and requirements outlined in the OME fish bioassay protocol document (Craig et al, 1983) unless otherwise noted.

The stock of test fish was obtained from a certified disease-free hatchery, Rainbow Springs Trout Farm, Thamesford, Ontario, for both the 1985 and 1986 studies. The fish were acclimated to the test conditions for at least 5 days prior to testing in 1985 with two different batches of fish used for the tests during that study. The mean weights of the batches were 0.93 ± 0.2 g and 1.09 ± 0.2 g, while their mean lengths were 40.9 ± 2.8 mm and 43.5 ± 2.4 mm, respectively. The test fish in 1986 were acclimated to test conditions for at least 23 days prior to use. The mean weight and length of those fish was 1.16 ± 0.4 g and 43.0 ± 4.0 mm, respectively.

A test concentration series of 100%, 65%, 32%, 18% and 10% Volume/Volume was used with mortality observations undertaken at test times of ½,1,2,4,24,48,72 and 96 h. Ten fish were exposed per test solution of 25 L in volume. A deviation from the OME test protocol involved the oxygenation of individual test solutions which did not have a dissolved oxygen concentration of greater than 7.0 mg/L prior to the start of the test. Pure oxygen was used rather than aeration in order to raise the effluent D.O. levels above 7.0

mg/L as quickly as possible, with the minimum of agitation and resultant loss of volatiles. In 1985, all full strength (100%) diffuser effluent samples were oxygenated with pure oxygen for 30 seconds, as was the case for the 65% test solution of the day 1 grab sample from the diffuser. In 1986, all full strength (100%) diffuser effluent samples were oxygenated with pure oxygen for 30 seconds, as was the case for the 65% test concentration of the day 4 - 5 composite sample from the diffuser. The dissolved oxygen levels in all test solutions exceeded 7.0 mg/L at the start of the tests.

Acute lethality results for all tests are presented as 96-h LC50s (concentrations of the samples lethal to 50% of the fish (i.e. the average fish) after a 96-h exposure), along with their 95% (or greater) confidence limits. The LC50's and confidence limits were calculated using the Spearman-Karber analyses (gives 95% confidence levels) or the binomial test method (gives 98% confidence levels for 10 test organisms/test solution). In all effluent samples, LT50's (time to lethality for 50% of the test fish) were calculated in the full strength mill effluent.

RESULTS

I. Acute Lethality

1. Field Exposure

In 1985, fish were exposed at control sites C1, C2 and test sites 1-9 inclusive (Figure 2). There was no mortality observed in either the smallmouth bass or fathead minnow exposures from August 12-16th of that year.

In addition to the test sites C1, C2 and 1-9 inclusive, sites 10 and 11 were also tested in 1986 (Figure 2). Brown trout were exposed at all sites while fathead minnow exposures were limited to sites C1, 1-6 inclusive and 11. There were two major portions of the river in which brown trout mortality was observed during the 96-h exposure. They included: (1) the area between the GLFP's Diffuser discharge and the Westford Turning Basin (Figure 3), and (2) much of the Mission River and up the Kam River to the Hwy. 61B swing bridge (Figure 4, Table 1). The only fathead minnow mortality occurred at site 11 (Table 2).

Significant fish mortalty was not observed until the 48-h exposure period, at which time the two areas of mortality within the river became evident (Figure 5). In turn, most of the mortality observed during the study had occurred within 72h (Figure 5).

2. Laboratory Bioassays

LC50 results for the Diffuser during the 1985 study ranged from 40-45.5% (Table 3), while more highly lethal levels of 24-33% occurred in the 1986 laboratory bioassays (Table 4).

FIGURE 3 :

FISH LETHALITY AT CAGE SITES IN THE KAM RIVER NEAR THE GREAT LAKES FOREST PRODUCTS PLANT.

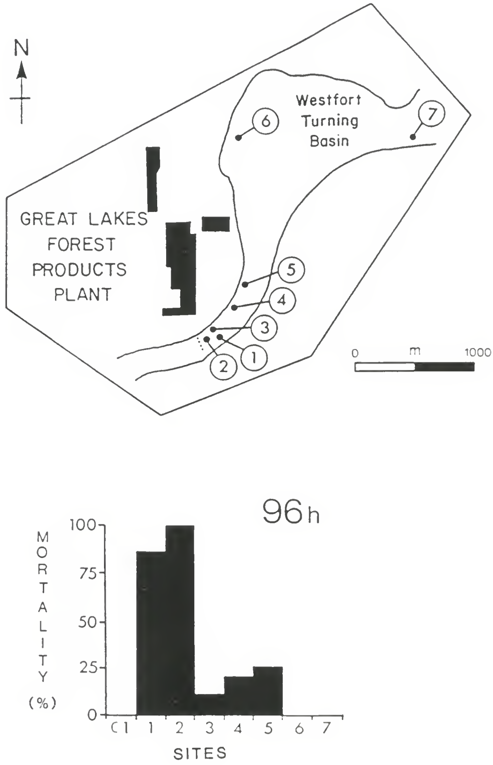


FIGURE 4:

FISH LETHALITY AT CAGE SITES IN THE KAM & MISSION RIVERS DOWNSTREAM OF THE GREAT LAKES FOREST PRODUCTS PLANT.

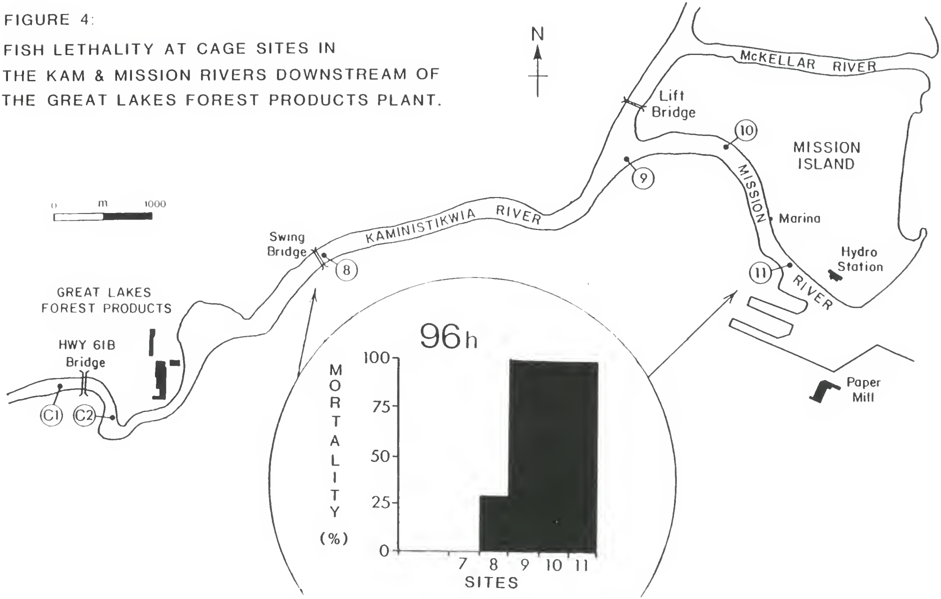


Table 1

Cumulative Mortality for Brown Trout in the Kaministikwia River during a 96-h Exposure (1986)

Site		Mortality (%) at				LT 50(h)[1]
No.	Description	24	48	72	96 h	
C-1	Control-upstream of Hwy #61A	0	0	0	0	-
C-2	Control-at GLFP's Water Intake	0	0	0	0	-
1	Downstream of Diffuser-60m - far shore site	0	4	46	84	78
2	Downstream of Diffuser-30m - central site	8	64	100	100	43
3	Downstream of Diffuser-60m - near shore site	4	7	7	11	-
4	Downstream of "Red" Intake - 30m	0	17	21	21	-
5	Turning Basin Inflow	0	0	13	25	-
6	Offshore of Clear Water Discharge - 75m	0	0	0	0	-
7	Turning Basin Outflow - southern shoreline	0	0	0	0	-
8	Hwy #61B Swing Bridge - mid river	0	0	0	28	-
9	300m Upstream of Mission R.- south shoreline	0	100	100	100	34
10	Mission R.- 900 m downstream of connection to Kam R. - north shore	0	100	100	100	34
11	Mission R.- 400 m downstream of Marina - east shoreline	0	71	100	100	43

---

[1] LT 50 - the estimated time in hours required to produce 50% lethality at each fish exposure site.

Table 2

Cumulative Mortality for Fathead Minnows in the Kaministikwia River during a 96-h Exposure (1986)

Site		Mortality (%) at				LT 50(h)[1]
No.	Description	24	48	72	96 h	
C-1	Control-upstream of Hwy #61A	0	0	0	0	-
2	Downstream of Diffuser-30m - central site	0	0	0	0	-
4	Downstream of "Red" Intake - 30m	0	0	0	0	-
6	Offshore of Clear Water Discharge - 75m	0	0	0	0	-
11	Mission R.-immediately upstream of Hydro plant	0	0	100	100	58

---

[1] LT 50 - estimated time in hours to produce 50% lethality at each fish exposure site.

FIGURE 5:

CUMULATIVE MORTALITY FOR BROWN TROUT IN THE KAMINISTIKWIA AND MISSION RIVERS DURING A 96-HOUR EXPOSURE

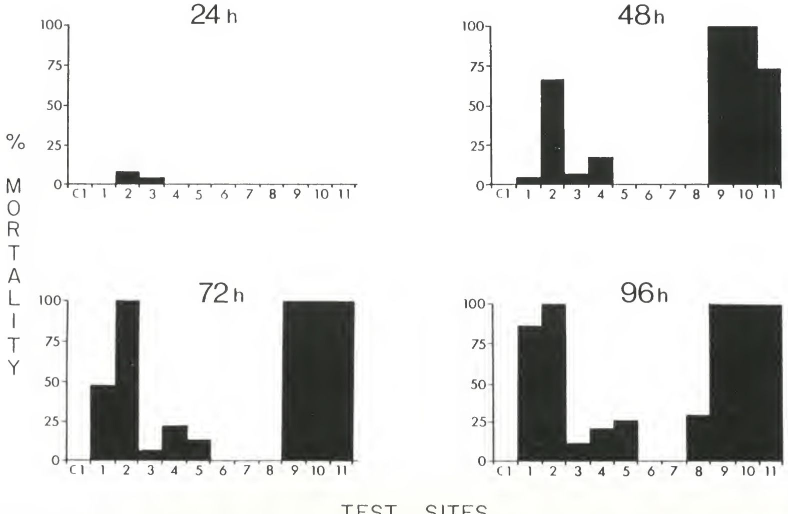


Table 3

Laboratory bioassay results for the Great Lakes Forest Products diffuser effluent from August 12-16, 1985 (Study Days 1-5, respectively), using Rainbow Trout Test Fish

			Fish Mortality/Test Solution		
Sample Type	Sample Day	Bioassay[1] LC50 (%v/v)	Effluent Concentration (%v/v)[3]	Fish Mortality (%)	LT50(h)[2] for 100% Effluent
24-h composite	1-2	43	100	100	10.5
		(48,38)[4]	65	100	
			32	10	
			18	0	
	2-3	40	100	100	10.5
		(47,34)	65	100	
			32	20	
			18	0	
24-h composite	1-2	43	100	100	10.5
		(48,38)	65	100	
			32	10	
			18	0	
24-h composite	2-3	45.5	100	100	10.5
		(65,32)	65	100	
			32	0	
grab	4	40	100	100	10.5
		(47,34)	65	100	
			32	20	
			18	0	

$\bar{x}$ - 42.8 S.D. - 2.5 N - 6 range - 40 - 45.5

---

[1] Results calculated using the Spearman-Karber Method or Binomial Test Method.

[2] LT50 - time required to produce 50% fish lethality in the 100% effluent.

[3] % v/v represents: volume of effluent/volume of dilution water, expressed as a percentage.

[4] Upper and lower 95% confidence levels, respectively.

Table 4

Laboratory bioassay results for the Great Lakes Forest Products diffuser effluent from August 11-15, 1986 (Study Days 1-5, respectively), using Rainbow Trout Test Fish

Sample Type	Sample Day	Bioassay[1] LC50 (%v/v)	Fish Mortality/Test Solution: Effluent Concentration (%v/v)[3]	Fish Mortality/Test Solution: Fish Mortality (%)	LT50(h)[2] for 100% Effluent
24-h composite	0-1	31 (38,25.5)[4]	100 65 32 18	100 100 60 0	10
24-h composite	1-2	24 (32,18)	100 65 32 18	100 100 100 0	5
24-h composite	2-3	27.5 (32,23)	100 65 32 18	100 100 80 0	10.5
24-h composite	3-4	33 (40.5,27)	100 65 32 18	100 100 50 0	10.5
24-h composite	4-5	33 (40.5,27)	100 65 32 18	100 100 50 0	3.25

LC50: $\bar{x}$ = 29.7%
range = 24-33%
N = 5

---

[1] Results calculated using the Spearman-Karber Method or Binomial Test Method.

[2] LT50 - time required to produce 50% fish lethality in the 100% effluent.

[3] % v/v represents: volume of effluent/total test volume, expressed as a percentage.

[4] Upper and lower 95% confidence levels, respectively.

All of the 1985 and 1986 samples from the Diffuser (designated as the "Combined Outfall/ by the region), failed to meet the Ontario Government toxicity test requirement for pulp and paper mill wastes of at least 50% fish survival in a 100% effluent concentration. The time for 50% of the fish (i.e. the average fish in the test population) to die in the full strength samples of the Diffuser effluent was calculated to be between 3.25 and 10.5 h (Table 3 and 4). These results indicate that effects can occur within a matter of hours rather than days.

Portions of the Clean Water and Diffuser/effluent samples were combined to produce a Total Mill Effluent sample, based on discharge volumes. All of those samples (two in 1985 and one in 1986) failed the federal regulatory test requirement for pulp and paper mill wastes (Appendix 1). On the other hand each of the Clean Water samples, used to produce the Total Mill Effluent samples, were not lethal to the test fish.

II. Chlorophenol Bioconcentration

1. Pentachlorophenol

All pentachlorophenol levels in fathead minnows and smallmouth bass in 1985 were similar to or below the detection level of 50 ng/g, with the highest single sample value of 75 ng/g (Appendix 2). In 1986, pentachlorophenol concentrations in fish were much higher relative to 1985 levels, with several values analyzed at over 500 ng/g (Appendix 3).

2. 2,4,6-Trichlorophenol

In both the 1985 and 1986 studies, the highest 2,4,6-trichlorophenol values were found in fathead minnows at site 2, 30 m downstream of the Diffuser. The highest levels were 766 ng/g ± 301 ng/g in 1985 (Table 5) and 846 ng/g ± 831 ng/g in 1986 (Table 6).

Table 5

Chlorophenol residues in composite samples of Fathead Minnows and Smallmouth Bass caged in the Kam River up and downstream of the GLFP's effluent diffuser during the period from August 12-16, 1985

1. Fathead Minnow Data

Site				Chlorophenol Residues (ng/g)	
No.	Description	No. of Composite Samples	% Fat Content[1]	2,4,6-Tri-chlorophenol[1]	Penta-chlorophenol[1]
-	Pre-exposure Fish from Lab.	5	7.2±1.2	nd	nd
C-1	Control-upstream of Hwy #61A	5	5.7±1.0	nd	nd
1	Downstream of Diffuser-60m - far shore site	5	6.5±0.5	nd	47±20[2]
2	Downstream of Diffuser-30m - central site	5	7.3±1.4	766±301	61±25[2]
3	Downstream of Diffuser-60m - nearshore site	5	6.1±1.1	366±119	35±14[2]
4	Downstream of "Red" Intake - 30m	5	6.1±0.8	247±179	39±19[2]
5	Turning Basin Inflow	4	6.7±1.1	183±42	nd
6	Offshore of Clear Water Discharge	4	6.8±0.4	125±45	nd
7	Turning Basin Outflow - southern shoreline	5	6.9±0.8	69±63[2]	nd
8	Hwy 61B Swing Bridge	5	7.1±0.7	77±40	nd
9	300m Upstream of Mission R.	5	6.9±0.8	50±36[2]	nd

Table 5 (Continued)

2. Smallmouth Bass

–	Pre-exposure Fish from Lab.	5	1.7±0.2	nd	nd
C-1	Control - upstream of Hwy #61A	5	2.0±0.3	nd	nd
2	Downstream of Diffuser-30m - central site	5	1.7±0.7	100±94	46±19[2]
4	Downstream of "Red Intake" - 30m	5	2.0±0.3	163±6	52±5[2]

[1] mean value and standard deviation

[2] for results in which the mean chlorophenol value is reported as near or below the detection level, as many as three (3) of the composite samples from that site had non-detectable chlorophenol values, and therefore they were given an arbitrary value of one-half (½) the detection level, in order to calculate a mean chlorophenol value and standard deviation for that site.

Note: (i) nd - not detected

(ii) 2,3,4 and 2,4,5 trichlorophenol species; 2,3,5,6 and 2,3,4,5 tetrachlorophenol species not detected in any fish samples

(iii) detection level >50 ng/g, except >100 ng/g for 2,3,4 trichlorophenol

Chlorophenol Analyses Undertaken		Detection Levels (ng/g)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,4,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5,6-Tetrachlorophenol	(2,3,5,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

Table 6

Chlorophenol residues in composite samples of Brown Trout and Fathead Minnows caged in the Kam River up and downstream of the GLFP's effluent diffuser during the period from August 11-15, 1986

1. Brown Trout

Site				Chlorophenol Residues (ng/g)	
No.	Description	No. of Composite Samples	% Fat Content[1]	2,4,6-Tri-chlorophenol[1]	Penta-chlorophenol
-	Pre-exposure Fish from Lab.	5	5.5±0.8	nd	nd
C-1	Control-upstream of Hwy #61A	5	4.6±0.4	nd	nd
1	Downstream of Diffuser-60m - far shore site	1	6.2	170	nd
2*	Downstream of Diffuser-30m - central site	3*	5.0±0.7	110±30	88±56
3	Downstream of Diffuser-60m - nearshore site	5	5.2±0.8	114±22	115±58
4	Downstream of "Red" Intake - 30m	4	5.5±0.6	139±30	215±174
5	Turning Basin Inflow	4	5.5±0.8	101±66	nd
6	Offshore of Clear Water Discharge	5	5.3±0.6	126±50	72±45[2]
7	Turning Basin Outflow - southern shoreline	5	5.9±0.6	134±49	146±56
8	HWY 61B Swing Bridge	4	5.7±0.5	170±34	255±172
9	Upstream of Mission River - 300m - south shoreline	5	5.0±0.3	162±65	128±79
10*	Mission River - 900m downstream of connection to the Kam River	5*	5.1±0.5	302±232	282±204
11*	Mission River - 400m downstream of Marina - east shoreline	3*	4.9±0.6	497±116	367±178

... Continued

Table 6 (Continued)

2. Fathead Minnows

Site No.	Site Description	No. of Composite Samples	% Fat Content[1]	Chlorophenol Residues (ng/g) 2,4,6-Trichlorophenol[1]	Chlorophenol Residues (ng/g) Pentachlorophenol[1]
-	Pre-exposure Fish from Lab.	-	-	-	-
C-1	Control - upstream of Hwy #61A	4	7.0±0.6	nd	nd
2	Downstream of Diffuser-30m - central site	4	-	846±831	404±343
4	Downstream of "Red Intake" - 30m	3	-	440±312	117±159
6	30m offshore from the "Clean Water" Discharge	4	-	150±28	54±58[2]

[1] mean value and standard deviation

[2] for results in which the mean chlorophenol value is reported as near or below the detection level, as many as three (3) of the composite samples from that site had non-detectable chlorophenol values and therefore they were given an arbitrary value of one-half (½) the detection level, in order to calculate a mean chlorophenol value and standard deviation for that site.

Note: (i) nd - not detected

(ii) 2,3,4 and 2,4,5 trichlorophenol species; 2,3,5,6 and 2,3,4,5 tetrachlorophenol species not detected in any fish samples

(iii) detection level >50 ng/g, except >100 ng/g for 2,3,4 trichlorophenol

(iv)* denotes analyses undertaken on fish which died during the exposure.

Chlorophenol Analyses Undertaken		Detection Levels (ng/g)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,4,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5,6-Tetrachlorophenol	(2,3,5,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

The 2,4,6-trichlorophenol concentrations in fish were greater than pentachlorophenol levels for both species in 1985 and the fathead minnows in 1986. At the extreme, tri-versus pentachlorophenol residues in fish were up to seven times greater at one site, and in no case were mean values of pentachlorophenol in fish at a site greater than for 2,4,6-trichlorophenol.

In both years, 2,4,6-trichlorophenol bioavailability to fish extended to the most distant survey station from the GLFP mill (i.e. to site 9 in 1985 and site 11 in 1986).

DISCUSSION

I. Acute Lethality

In 1986, acute lethality was measured in two stretches of the Kam River (one of which includes the Mission River) as well as in laboratory bioassays of the mill's final effluent. Each case is examined in an attempt to determine the source and/or critical factors affecting lethality.

1. The Lower Kam and Mission Rivers

The stretch of the Kam River under discussion extends downstream from the Hwy. 61B swing bridge to its confluence with the Mission River and in turn down the Mission to the Hydro property (Figure A ~~B~~). Twenty-eight percent of the fish died at the swing bridge site over 96 h, while all of the fish exposed at the other three sites died within 48 h. The fish mortality was due to depressed oxygen levels within that river reach. The critical level of dissolved oxygen for brown trout mortality was 3.0 mg/L, and all stations that had D.O. below that level produced brown trout mortality within 24 h.

The only fathead minnow cage in the area had no fish mortality at a dissolved oxygen level of 2.7 mg/L, on test day 3, and complete mortality 24 h later, with a 1.6 mg/L dissolved oxygen concentration. The lowest oxygen levels measured in the Mission River area during the study were 0.5 mg/L at site 9 and 0.8 mg/L at site 10, on study day 3 (Table 7). It should be noted that the "critical level" in this study related to acute lethality only and the no effect level as it relates to sublethal responses by aquatic biota would most likely be at a D.O. of 5.0 mg/L or greater (ie. the provincial water quality objective for cold water fish).

Those dissolved oxygen levels (0.5-2.7 m/L), which are considered as very low, are consistent with values measured in this stretch of river before and after this study. Similar levels of less than 1.0 mg D.O./L at those sites were documented in May 14, July 19 and August 3, 1977 (OME, 1978a); June 16 and August 14, 1980 (OME, 1981); August 4, 10, 24, 31, September 9, 14 and 21, 1981 (OME, 1982) and June 17, July 29 and August 4, 1987 (OME, 1987). It appears that very severe conditions can occur during the late spring, summer and early fall, especially during years when the pulp and paper mill is running at full capacity (i.e. 1980, 1981 and 1987). Several other factors also have a bearing, which include precipitation levels during critical times, the current water levels in the upper watershed and minimum water levels which must be maintained upstream of the Hydro dams. For fish kills to occur, important factors include the degree of the dissolved oxygen depression, the extent of low D.O. levels throughout the water column, duration of stressful conditions and the time of year insofar as it relates to spawning runs and fish migrations.

Table 7

Dissolved Oxygen Levels in the Kam River upstream and downstream of the Great Lakes Forest Products (GLFP) diffuser during the period from August 11-15, 1986 (Study days 1-5)

Site		Dissolved Oxygen (mg/L) on Study Days				
No.	Description	1	2	3	4	5
C-1	Control-upstream of Hwy. #61A	7.2	8.8	8.0	8.6	8.3
C-2	Control-at GLFP's Water Intake	6.9	9.1	8.6	8.6	8.0
1	Downstream of Diffuser-60m - far shore site	7.8	8.3	8.0	8.0	7.5
2	Downstream of Diffuser-30m - central site	7.3	8.9	7.8	7.6(6.9)	7.9(5.9)
3	Downstream of Diffuser-60m - near shore site	7.5	8.6	7.6	8.3	8.0(7.8)
4	Downstream of "Red" Intake - 30m	7.2	9.0	7.8	8.5(8.0)	7.0(6.8)
5	Turning Basin Inflow	7.3	8.1	7.9	8.2	7.6
6	Offshore of Clean Water Discharge - 75m	5.2	4.1	3.4	5.0	3.8
7	Turning Basin Outflow - southern shoreline	7.2	4.2	5.0	4.8	4.7
8	Hwy #61B Swing Bridge - mid river	6.0	3.4	3.6	2.6	3.8
9	Upstream of Mission R. - 300m - south shoreline	3.8	2.4	0.5	-	-
10	Mission R.-upstream of Marina - 600 m - north shore	3.6	3.1	0.8	-	-
11	upstream of Hydro plant Mission R.-immediately	4.5	4.3	2.7(2.5)	1.6	-

Note: Values in brackets represent dissolved oxygen levels measured in the cages.
- Denotes that site not sampled because all test fish had died on the previous day.

In years in which D.O. levels are still depressed, but less severely than in 1987, it is not uncommon to measure surface water levels at below the critical D.O. level of 3.0 mg/L in the Kam River. Dissolved oxygen levels below 3.0 mg/L in the stretch of river under consideration have been recorded in every year from 1976-87 except 1984 and 1985.

Surface water dissolved oxygen is only a warning of possible problems and the D.O. profile at a site must be considered in any situation regarding fish life. Based on work by the Ministry's River Systems Section, it was found that oxygen levels were only depressed below 3.0 mg/L for the first 2 to 3 metres of the average 8 m depth at sites 8-11 of this study (Klose, 1988). Hence a zone of passage and accommodation was available along the river bottom for fish indigenous to this part of the river during the August 11-15, 1986 study. However, this is not always the case. The only other year in which D.O. profiles were reported (1987), fish throughout the water column at certain sites would have been severely stressed. In fact in that year, at least one fish kill did occur (observed May 17/87 at 1400 hours).

From the 1987 data compiled by the Northwestern Region on D.O. profiles, we have determined that on 17 of 45 study days, water quality was severely impaired in regard to D.O., for at least one of the sample sites in the study area downstream of GLFP. A site is considered to be severely impaired when the D.O. values measured in profile at 1 m intervals through the complete water column at the site are all less than 3.0 mg/L. As indicated previously, a D.O. exposure of less than 3.0 mg/L was found to be lethal to trout in this study over a 24-h period.

Severe impairment in stretches of the river downstream of the swing bridge extended over distances varying from 1.0 to 4.3 km, on 12 of 45 days during the summer of 1987. The first observation of severe impairment at a site occurred on May 13, 1987 and severe impairment in a stretch of the river (ie. 2 or more adjacent sites) happened May 14, 1987. A fish kill in that area of the Kam River coincided with those low oxygen measurements. At the worst of the two sites, D.O. levels in the water column ranged from 0.6-1.2 mg/L. That incident in May also involved the longest stretch of time in which severe impairment was measured, i.e. from May 16 (0900h) to May 18 (1025h). During periods in which the entire water column at a site had D.O. levels of less than 3.0 mg/L, a zone of passage was not considered to exist at that site. The D.O. problem was so severe in the Westfort Turning Basin during 1987 that the company considered a plan to oxygenate the river as a remedial measure. However, that plan was never carried out.

The only site at which fish mortality occurred in our study due to low dissolved oxygen levels and which was monitored for D.O. profiles in 1987, was station 9, near the confluence of the Kam and Mission Rivers. The water column was considered severely impaired at that site on May 14, 16, 17, 18 and July 21 and 22 during the 1987 study, and fish mortality would have been expected at any depth during those two extended periods of impairment.

During periods of high mortality in the lower Kam and Mission Rivers, toxicants contained in the mill effluent were unlikely to be the direct cause of acute lethality in this study. The highest effluent concentration, during the first 48 h at sites 9, 10 and 11 and over 96 h at site 8 was between 8-11%, based on conductivity (Appendix 4). Those levels are less than half of the average LC50 of 29% for the mill diffuser effluent. Furthermore, resin acids, the principal family of toxicants in pulp mill wastes, were detected at low levels at sites 8-11 over the first 48 h of the study (Table 8).

In the 1985 in situ fish exposure in the Kam River, the lack of fish mortality coincided with D.O. levels equal to or greater than 4.9 mg/L at all cage sites. These results are consistent with observations that acute mortality occurred at oxygen levels of 3.0 mg/L or lower. Resin acid levels in the river in 1985 were similar to levels in 1986 (Tables 8 and 9).

Table 8

Resin Acid concentrations (µg/L) in the Kam River up and downstream of the Great Lakes Forest Products diffuser on August 11-13, 1986 (Study Days 1-3, respectively)

Study Day/Resin Acid Species	Exposure Site Resin Acid Levels (µg/L) Concentrations at Study Sites										
	1	2	3	4	5	6	7	8	9	10	11
Day 1											
Pimaric	nd	14	nd	14	10	nd	10	nd	nd	nd	nd
Sandaracopimaric	nd	18	nd	17	12	nd	12	12	nd	nd	nd
Isopimaric	nd	31	nd	33	23	11	24	21	nd	nd	nd
Abietic	nd	46	nd	230	168	42	158	104	nd	nd	nd
Dehydroabietic	nd	150	nd	150	105	32	116	80	15	13	13
Day 2											
Pimaric	14	13	10	13	nd	nd	12	12	nd	nd	nd
Sandaracopimaric	18	15	11	14	10	nd	15	nd	nd	nd	nd
Isopimaric	35	32	25	32	20	14	30	23	15	12	nd
Abietic	280	245	152	230	90	65	90	120	40	30	nd
Dehydroabietic	150	130	100	128	90	43	100	65	37	30	nd
Day 3											
Isopimaric	nd	13	nd	12	10	nd	11	nd	nd	nd	nd
Abietic	28	78	15	70	32	nd	37	nd	nd	nd	nd
Dehydroabietic	25	55	21	50	43	nd	40	nd	20	14	nd

Note: The detection level for all resin acids was 10 µg/L
nd - not detected
Of the ten resin acid species analyzed for in the river samples of this study, Palustric, Levopimaric, Neoabietic, Monochlorodehydroabietic and Dichlorodehydroabietic Acids were not detected.

Table 9

Resin Acid concentrations (µg/L) in the Kam River up and downstream of the Great Lakes Forest Products diffuser on August 12-13, 1985 (Study Days 1-2, respectively)

Study Day/Resin Acid Species	Exposure Site Resin Acid Levels (µg/L) Concentrations at Study Sites								
	1	2	3	4	5	6	7	8	9
Day 1									
Pimaric	15	20	nd	15	15	nd	nd	nd	nd
Sandaracopimaric	15	20	nd	15	15	nd	nd	nd	nd
Levopimaric	15	20	nd	15	15	nd	nd	nd	nd
Isopimaric	15	20	nd	15	15	nd	nd	nd	nd
Abietic	190	265	40	110	210	15	35	20	10
Dehydroabietic	100	125	20	90	90	15	20	20	10
Monochlorodehydroabietic	12	1	nd	nd	10	nd	nd	nd	nd
Day 2									
Pimaric	15	20	-	nd	nd	10	10	10	nd
Sandaracopimaric	20	20	-	nd	nd	10	10	10	nd
Levopimaric	20	25	-	nd	nd	10	10	10	nd
Isopimaric	20	25	-	nd	nd	10	10	10	nd
Abietic	140	260	-	nd	10	40	55	30	10
Dehydroabietic	100	140	-	nd	15	30	50	40	25

Note: The detection level for all resin acids was 10 µg/L
nd: not detected
Of the ten resin acid species measured in the river samples of this study, only Palustric, Neoabietic and Dichlorodehydroabietic Acids were not detected.
-: not sampled.

Acute lethality due to contaminants in the effluent was not expected. Effluent concentrations in the river never exceeded 10% based on conductivity (Table 10) while the LC50 for the mill diffuser effluent averaged 42.8% during the study (Table 3).

2. The Kam River at the GLFP's Mill

The stretch of river referred to in this part of the report extends from the GLFP's mill diffuser downstream to the Westfort Turning Basin inflow (Figure 3~~2~~).

Fish mortality in this stretch of river was due to a combination of factors including the chemical toxicants within the mill effluent and associated bacterial growth; with the latter factor becoming a greater influence as the exposure progressed. Within 48 h, there was 64% mortality at cage 2. At that time and on each succeeding day thereafter, attempts were made to clean the exposure cages by brushing the bacterial growth from the net tops, sides and bottoms. Such a procedure was required in order to allow for a good exchange of water into and out of the cages. The lowest D.O. level measured at sites 1-5 during the study was 5.9 mg/L (in the cage at site 2 on day 5). Therefore, D.O. levels at those sites were well above lethal levels of <3.0 mg/L during the study.

During the net cleaning procedure, broken clumps of the bacterial growth passed into the cages and were in suspension or settled on the cage bottom. After the initial cleaning (i.e. beyond 48 h), the principal cause of fish mortality in the cages at sites 1-5 inclusive was likely due to the fish having their gills clogged by clumps of the bacterial slime and/or related disease problems.

Diffuser effluent concentrations of between 9-18% at site 2 were some of the highest levels recorded in the river during the study (Table 10). Their effect on fish mortality at dissolved oxygen levels which were for the most part above

Table 10

Conductivity levels (umhos/cm) and calculated Mill Effluent concentrations (%) at sites in the Kam River where acute lethality was observed immediately downstream of Great Lakes Forest Products' diffuser discharge on August 11-15, 1986 (Study Days 1 - 5 respectively).

Site		Conductivity & Related Effluent Concentrations (in brackets)[1] on Study Days				
No.	Description	1	2	3	4	5
1	Downstream of Diffuser-60m - far shore site	275(10%)	290(13%)	310(16.5%)	220(11.5%)	310(11.5%)
2	Downstream of Diffuser-30m - central site	255(9%)	273(12%)	235(11%)	305(18%)	300(11%)
3	Downstream of Diffuser-60m - near shore site	-	195(7.5%)	260(13%)	200(10%)	135(2.5%)
4	Downstream of "Red" Intake - 30m	250(8.5%)	240(10%)	255(12.5%)	165(6.5%)	310(11.5%)
5	Turning Basin Inflow	205(6.5%)	125(3%)	235(11%)	195(8.5%)	210(6.5%)
	Other Pertinent Sites					
C-2	Control - at GLFP's Water Intake	72	72	85	75	85
-	Diffuser Effluent (Full Strength)	2150	1750	1450	1350	2000

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[1] Effluent Concentrations based on Relative Conductivity (C_R) using the Formula $C_R = \frac{C_ts - C_c}{Ce - C_c}$ where C_ts = conductivity at a specific test site,

C_c = conductivity at a river control site,

and C_e = conductivity of the full strength effluent sample.

Note: All values obtained from grab samples.

7.0 mg/L would not have had a major impact on fish lethality, based on bioassay results of the diffuser effluent measured in the lab (Table 4). The average concentration of effluent at site 2 was 12%, by volume, while no fish mortality was observed in laboratory bioassay concentrations of 18%.

II. Chlorophenols

1. The Mill Effluent

Chlorophenols are common to all bleached kraft mill effluents (BKME) in varying amounts. Cherwinsky and Murray (1986) measured chlorophenols in all six BKME's in northwestern Ontario (including the GLFP, Thunder Bay division plant in this study). They found 2,4,6-TCP concentrations ranging up to 16,000 ng/L; 2,3,5,6-TTCP up to 1600 ng/L and maximum levels of PCP at 2250 mg/L. Not only can CP's differ between mills but levels at the same mill may vary widely. Concentrations of 2,4,6-TCP and PCP in the GLFP mill effluent was significantly higher in 1986 versus 1985 (Tables 11 and 12). Furthermore, no PCPs were detected in the diffuser discharge on a day-to-day basis in 1985, while in 1986 the mean PCP level over 5 days was 30,200 ng/L ± 4,500 ng/L. That is not to say, that no PCPs were discharged during the 1985 study. There was a large pulse of PCP detected in the surface waters six hours after sampling the effluent discharge, immediately downstream of both major outfalls during a storm event on study day 1. At the water surface in the Westfort Turning Basin, 150 m from the Clean Water discharge, PCP was measured at 210,000 ng/L. A surface sample collected at site 2, 30 m downstream of the Diffuser outfall, had a PCP concentration of 24,000 ng/L. Based on conductivity, a Diffuser effluent sample discharged at the river bottom is diluted 10:1 by the time it reaches the river surface. In such a case, the 24,000 ng/L level of PCP measured at the surface would have been a result of a 240,000 ng/L level discharged from the Diffuser sewer on the river bottom. In regard to 2,4,6-TCP in the effluent, 4 of 5 samples in 1986 had levels above 23,000 mg/L, while 1985 levels were all less than 16,000 mg/L (Tables 11 & 12).

2. Chlorophenols in the River

On a day-to-day basis, 2,4,6-TCP, 2,3,5,6-TTCP and PCP concentrations were found to be more consistently above detection levels in 1986 than in 1985. For example, 3 of 27 river samples in 1985 had detectable levels of PCP while 16 of 48 samples had detectable levels in 1986. Similarily 16 of 48 river samples in 1986 had detectable levels of 2,3,5,6-TTCP while TTCP was not found in any 1985 samples. These results can be explained by the lower river flows in 1986 (17 m^3/s versus 40-50 m^3/s in 1985), in combination with higher effluent concentrations.

Voss and Yunker (1983) found 80 ng/L of 2,4,5-TCP as far as 110 km downstream of a pulp mill in B.C. Levels of 2,4,6-TCP in this study were measured at site 11, 8 km downstream of the mill diffuser in 1986, and as far downstream as was tested in 1985, i.e. at site 9. The maximum 2,4,6-TCP values at site 9 in 1985 and 1986 were 550 and 1360 ng/L, respectively. PCP's were found in river samples at site 9, 5 km downstream of the diffuser in 1986 (Table 13) and were found only in the immediate area of the discharges in 1985 (Table 14).

3. Chlorophenol Sources

The principal chlorophenol contaminants measured in the mill effluent, river water and fish samples of this study were 2,4,6-trichlorophenol and pentachlorophenol. The 2,4,6-TCP is most likely a byproduct of the kraft mill bleaching process (Lindstrom and Nordin, 1976; Claeys et al, 1976). The occurrence of pentachlorophenol in the effluent would be more

Table 11

Chlorophenol concentrations in daily grab samples of GLFP's effluents collected August 12-16, 1985 (Study Days 1-5, respectively)

1. DIFFUSER EFFLUENT

Chlorophenol Species	Chlorophenol Concentrations (ng/L) on Study Days				
	1	2	3	4	5
2,4,6-Trichlorophenol	8,000	NA	11,600	16,000	11,000
2,3,4,5-Tetrachlorophenol	nd	NA	nd	nd	nd
Pentachlorophenol	nd	NA	nd	nd	nd

2. CLEAN WATER EFFLUENT DISCHARGE: Not analyzed

Table 12

Chlorophenol concentrations in daily grab samples of GLFP's effluents collected August 11-15, 1986 (Study Days 1-5, respectively)

1. DIFFUSER EFFLUENT

Chlorophenol Species	Chlorophenol Concentrations (ng/L) on Study Days				
	1	2	3	4	5
2,4,6-Trichlorophenol	46,000	4,660	30,000	23,000	32,000
2,3,4,5-Tetrachlorophenol	nd	NA	nd	nd	200
Pentachlorophenol	31,000	31,000	22,000	35,000	32,000

2. CLEAN WATER EFFLUENT DISCHARGE

Chlorophenol Species	Chlorophenol Concentrations (ng/L) on Study Days				
	1	2	3	4	5
2,4,6-Trichlorophenol	LA	1,400	1,070	690	520

Chlorophenol Analyses Undertaken		Detection Levels (ng/L)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,3,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5,6-Tetrachlorophenol	(2,3,5,6 TTCP)	50
2,3,4,6-Tetrachlorophenol	(2,3,4,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

Note: NA - Not Available   nd - not detected

The retention time for the analyses of 2,3,4,6- and 2,3,4,5-Tetrachlorophenol is the same; hence, 2,3,4,5-TTCP results also include 2,3,4,6-TTCP levels.

LA - Laboratory Accident

Table 13

Chlorophenol concentrations (ng/L) in the Kam River up and downstream of the Great Lakes Forest Products diffuser on August 11-15, 1986 (Study Days 1 - 5 respectively)

STUDY DAY/ Chlorophenol Species	Concentrations (ng/L) at Study Sites												
	C-1	C-2	1	2	3	4	5	6	7	8	9	10	11
DAY 1													
2,4,6-TCP	nd	nd	640	930	nd	950	930	380'	nd	550	260'	160'	nd
2,3,4,5-TTCP	nd	nd	50'	70'	nd	80'	70'	nd	70'	nd	nd	nd	nd
Penta CP	nd	nd	nd	100	nd	100'	120'	nd	80'	50'	nd	nd	nd
DAY 2													
2,4,6-TCP	nd	nd	1190	920	590	700	800	440	1335	640	nd	540	400'
2,3,4,5-TTCP	nd	nd	nd	nd	60'	80'	nd	nd	80'	nd	nd	nd	nd
Penta CP	nd	nd	60'	60'	70'	120'	nd	nd	90'	nd	130'	nd	nd
DAY 3													
2,4,6-TCP	nd	nd	1290	1290	-	1610	1060	nd	1310	410'	1360	980	610
2,3,4,5-TTCP	nd	nd	nd	60'	-	nd	nd	nd	nd	nd	nd	nd	nd
DAY 4													
2,4,6-TCP	nd	nd	-	810	580	390'	420'	410'	560	360'	-	-	550
2,3,4,5-TTCP	nd	nd	-	70	50'	nd	nd	nd	nd	nd	-	-	nd
Penta CP	nd	nd	-	nd	80'	nd	nd	nd	60'	nd	-	-	nd
DAY 5													
2,4,6-TCP	nd	nd	1130	1490	700	730	810	710	920	830	-	-	-
2,3,4,5-TTCP	nd	nd	110'	90'	nd	nd	nd	50'	70'	80'	-	-	-
Penta CP	nd	nd	120'	120'	nd	50	nd	nd	nd	nd	-	-	-

Chlorophenol Analyses Undertaken		Detection Levels (ng/L)
2,3,4 - Trichlorophenol	(2,3,4 TCP)	100
2,3,5 - Trichlorophenol	(2,4,5 TCP)	50
2,4,6 - Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5 - Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5,6 - Tetrachlorophenol	(2,3,5,6 TTCP)	50
2,3,4,6 - Tetrachlorophenol	(2,3,4,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

nd - not detected
- - sample not analyzed
' - all chlorophenol concentrations <500 ng/L are tentative and are provided as information only.

Note: The retention time in the analyses for 2,3,4,5 and 2,3,4,6-tetrachlorophenol is the same; hence 2,3,4,5 TTCP results also include 2,3,4,6 TTCP levels.

Table 14

Chlorophenol concentrations (ng/L) in the Kam River up and downstream of the Great Lakes Forest Products diffuser on August 12, 14 and 16, 1985 (STUDY DAYS 1, 3 and 5 respectively)

EXPOSURE SITE CHLOROPHENOL LEVELS (ng/L)

STUDY DAY/ Chlorophenol Species	Controls		Concentrations (ng/L) at Study Sites								
	C-1	C-2	1	2	3	4	5	6	7	8	9
DAY 1											
2,4,6-TCP	nd	nd	nd	nd	900	nd	nd	nd	400	400	270
2,3,4,5-TTCP	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Penta CP	nd	nd	nd	nd	24,000	nd	nd	210,000	nd	nd	nd
DAY 3											
2,4,6-TCP	nd	nd	nd	930	1,200	1,800	1,000	500	750	600	550
Penta CP	nd	nd	nd	nd	nd	50	nd	nd	nd	nd	nd
DAY 5											
2,4,6-TCP	nd	nd	1,400	nd	nd	nd	nd	nd	nd	900	50

Chlorophenol Analyses Undertaken	Detection Levels (ng/L)
2,3,4-Trichlorophenol	100
2,3,5-Trichlorophenol	50
2,4,6-Trichlorophenol	50
2,3,4,5-Tetrachlorophenol	50
2,3,5,6-Tetrachlorophenol	50
2,3,4,6-Tetrachlorophenol	50
Pentachlorophenol	50

Note: The retention time in the analyses for 2,3,4,5- and 2,3,4,6-tetrachlorophenol is the same; hence 2,3,4,5 TTCP results also include 2,3,4,6 TTCP levels.

nd - not detected

Study Days	Dates
DAY 1	August 12, 1985
DAY 3	August 14, 1985
DAY 5	August 16, 1985

closely related to use as a preservative for pulp mill processing materials (Jones, 1961) or as a slimicide, for PCP synthesis in the bleachery only occurs to a minor degree (Paasivirta *et al*. 1985). The two large pulses of PCP measured in the river at up to 4,000 times normal levels during the storm event of August 15/85 (Table 14) made it appear that a slug treatment of PCP was being added to the process streams of the mill to control fungal growth at the time of sampling (which was approximately 6 hours after our grab sample of effluent was collected). However, according to Great Lakes Forest Products, a PCP-based slimicide has not been used in the plant for at least 10 years.

III. Environmental Effects

1. Acute Lethality

Several short-term lethality bioassays have been performed with sodium pentachlorophenate (NaPCP), the sodium salt of PCP, on various minnow species. Concentrations of 320,000 - 400,000 ng NaPCP/L produced greater than 50% fish mortality in 24h or less (Goodnight, 1942; Crandall and Goodnight, 1959). Bioassays using rainbow trout (*Salmo gairdneri*), produced an LC50 of 250,000 ng NaPCP/L, within 7-9 hours (Alexander and Clark , 1978). A peak PCP concentration of 210,000 ng/L was observed in this study at the Clean Water Discharge (site 6) on study day 1, 1985. No fathead minnow mortality was observed during that event. The time required to produce an LC50 for fathead minnows at that concentration would have been 48h (Slooff, 1982). Such a time requirement exceeded the actual exposure time by at least 24h, and most likely 40h or more, based on observations and results found in the literature.

The continuous minimum exposure level required to produce an LC50 in 96h (at pH 7.0) would have been at least 50,000 ng NaPCP/L (Davis & Hoos, 1975). That concentration/exposure level relationship was not approached in this study and therefore, as expected, there was no fish mortality during 1985 and the mortality which was observed in 1986 was most likely due to other factors.

The 96h LC50 for 2,4,6-TCP was 450,000 ng/L at pH 6.4 and 2.6 M ng/L at pH 7.7 using rainbow trout (PPRIC, 1979). Those values far exceeded levels present in the river during the time of this study. Therefore 2,4,6-TCP would not likely have had an appreciable effect on acute lethality of the fish.

2. Bioconcentration

Pentachlorophenol is a moderately lipophilic and relatively non-persistent environmental contaminant (McKee, 1984). Its uptake in fish is very rapid (Glickman et al, 1977: Kobayaski and Akitake, 1975), principally byway of the gills (Nimii and McFadden, 1982). The other highly chlorinated phenols, the tri-and tetra-species, act in a similar fashion, with PCP being the most toxic and persistent of the group.

a) 1985 - Results

The levels of pentachlorophenol in fathead minnows in 1985 demonstrated a localized effect near the mill with detectable levels of PCP in two or more replicate samples at sites 1-4 only. On the other hand, 2,4,6-trichlorophenol levels in fish downstream of the mill were ubiquitous, with fish exposed at sites 2-9 having step-wise decreases in mean levels (766,366,247,183,125, 69,77 and 50 ng/g) at progressively greater distances downstream of the mill (Table 5).

The bioconcentration factor (BCF), which is a measure of the body burden of a compound in fish relative to the exposure level of that compound; was calculated for fathead minnow uptake of 2,4,6-TCP at each exposure site. The BCFs of 2,4,6-TCP decreased in a step-wise progression of plateaus, with individual values for sites 2-9 of 2349, 516, 400,523, 683, 184, 121 and 172, respectively. The high value at site 2 and two plateaus (i.e. between 400-683 for sites 3-6 and 121-172 for 7-9) may be due to a number of factors affecting the efficiency of contaminant uptake. Spehar et al (1985) found BCF's decreased from 1066, 434, 426 to 281 as test solution pH's increased from 6.5 through to 8.5. However, pH levels at progressive distances downstream in this study did not change appreciably (Appendix 11 and 12). Kaiser and Valdimanis (1982) concluded that pH and the ionic strength may influence the environmental effects and pathways of ionizing compounds such as PCP, in turn affecting BCF's by several orders of magnitude. However, no relationship could be found between conductivity, sodium, alkalinity, solids or COD and BCF's in this study.

PCP and 2,4,6-TCP concentrations were also measured in smallmouth bass at sites 2 and 4 downstream of the diffuser. At site 2, the fathead minnows contained significantly greater 2,4,6-TCP levels than the smallmouth bass ($p>0.01$). Mean TCP concentrations in the fathead minnows were 7 and 1.5 times greater than in the smallmouth bass exposed at sites 2 and 4, respectively. Also, there were great differences in their lipid content, which may have played a role in contaminant differences between the species. The lipid content in individual composites of the smallmouth bass ranged from 1.68-2.40% (wet weight) while levels from 4.96-9.12% (wet weight) were present in the fathead minnows. When the contaminant data was normalized in regard to lipid levels, 2,4,6-TCP levels in fatheads changed from greater than 7 to less than 2 times the levels in bass at site 2 and from 1.5 to ½ the levels in bass at site 4.

b) 1986 Results

The 2,4,6-TCP levels in brown trout were fairly consistent throughout much of the study area. There was no significant difference in levels for brown trout exposed at sites 2-9. However, there was a significant difference in levels for fish at sites 10 and 11, with levels in the Mission River fish significantly greater than levels at all other sites. (Table 15).

BCF's ranged from 101 to 320 in brown trout at sites 1-9, based on mean 2,4,6-TCP levels in those fish. Those levels are similar to a BCF of 310 in the golden orfe (Leuciscus idus), European cyprinid (Freitaq, 1982) and "about 300" in the flag fish (Jordanella floridae), (Landner, 1979). On the other hand, the BCF's at sites 10 and 11 were 539 and 1255, respectively, indicating that fish at those two sites were more efficient accumulators of TCP.

Mean PCP concentrations in brown trout were also elevated slightly at site 10 and more noticeably at site 11 relative to fish at the other sites. The elevated levels at sites 10 and 11 are not due to higher elevated exposure levels of CP's relative to other sites, nor the time of exposure. In fact, the exposure duration at those (10 and 11) sites was 48h prior to death, while fish from all other sites except no. 2 were sacrificed and analyzed after a 96h exposure. A possible explanation for the greater bioconcentration of CP's by fish at sites 10 and 11 relative to the others, was due to the low oxygen levels at those two sites. Low oxygen levels would have resulted in increased respiration rates of the fish, allowing for greater CP loadings to pass over the gills per unit time, and hence the opportunity for greater uptake rates. In conjunction with greater

Table 15: A comparison of 2,4,6-Trichlorophenol concentrations in Brown Trout exposed at different sites in the Kam River up and downstream of the GLFP's plant, using the Least Significant Difference Multiple Range Test (with 95% confidence levels)

Site No.	Site Description	Number of Samples	Mean Value	Homogeneous* Groups
-	Pre-exposure Fish	5	25	a
C-1	Control-upstream of Hwy. #61	5	25	a
5	Turning Basin Inflow	4	101	a,b
2	Downstream of Diffuser 30m - central site	3	110	a,b
3	Downstream of Diffuser - nearshore site	5	114	a,b
6	Offshore of Clear Water Discharge	5	126	a,b
7	Turning Basin Outflow - shouthern shoreline	5	134	a,b
4	Downstream of "Red" Intake - 30m	4	139	a,b
9	300m Upstream of Mission River - south shoreline	5	162	b
8	Hwy 61B Swing Bridge - mid river	4	170	b
10	Mission River - 900m downstream of connection to the Kam River	5	302	c
11	Mission River - 400m downstream of Marina east shoreline	3	497	d

*Note:

1) "a" signifies that 2,4,6-TCP values at all sites represented by an "a" are not significantly different from each other 95% of the time. Likewise for "b" designates.

2) "a" and "b" designations for a site (e.g. site 5) signifies that its mean value is not significantly different from all other "a" and "b" site means.

3) The "a" only for site C-1 and "b" only for site 9 signifies that there is a statistically significant difference in their mean 2,4,6-TCP values at the 95% confidence level (i.e. 95 times out of 100 times tested).

Note:
Site 1 had only one sample (170 ng/g) and therefore was not included. TCP levels were not detected in samples from the first two sites and therefore an arbitrary value of one half of the detection level was assigned. Raw data is presented in Section 1 of Appendix 3.

CP uptake and the lack of oxygen available to the fish for normal body functions, chlorophenol metabolism and elimination known to occur in fish (Kobayashi and Akitake, 1975; Glickman et al, 1977) would most likely have been impaired. The only other fish to have died prematurely (also within 48h) were at site 2. They did not have elevated CP levels relative to fish at the other sites from 1-9 and oxygen was not a critical factor in their demise. Hence increased respiration rates were not likely experienced, CP uptake was not enhanced, nor was their metabolism and elimination greatly curtailed.

Fathead minnows in 1986 appear to be better accumulators of CP's than brown trout, and the differences can not be accounted for by differences in lipid content between the species.

The mean 2,4,6-TCP and PCP levels for fathead minnows at site 2 were 7.5 and 3.5 times greater than values for brown trout at that site. (Table 6). At progressive distances downstream (sites 4 and 6), the variability of fathead minnow data decreased and values converged with those of the brown trout. In no case could a statistically significant difference in values be differentiated because of the great variability in fathead minnow data. It should also be noted that more non detectable levels of CP's were measured in fathead minnow samples for which more than 50% of the replicates were found to have detectable CP levels. The reason may be that fathead minnow body tissue appears to decompose at a much faster rate than brown trout or smallmouth bass. The fatheads were observed to release body fluid within an hour after death, while brown trout wrapped in foil and on ice (not frozen) maintained all fluid and much of their colour for several hours.

c) A COMPARISON OF 1985 AND 1986 RESULTS

Fathead minnows were used in 1985 and 1986, and data is only available for 3 sites in both study years due to lack of fish in 1986. At sites 2 and 6, mean TCP levels were very similar in 1985 and 1986 (Table 16), while at site 4, the mean level in 1986 was nearly double the 1985 value. The difference at site 4 was not statistically significant and not beyond what would be expected for within species differences.

PCP values for individual fathead minnow samples at sites 2 and 4 in 1986 were much greater than in 1985. However, the variability in fathead minnow data at a site during an exposure was so large as to preclude the possibility of making a comparison of the 1985 and 1986 PCP results.

d) A COMPARISON OF INDIGENOUS AND IN-SITU EXPOSED FISH

Young-of-the-year walleye (Stizostedion vitreum) samples were collected by divers in an area bounded by the mill diffuser and Westfort Turning Basin in August, 1986. PCP and 2,4,6-TCP levels in 3 composites of those fish (Table 17) were compared to levels in fathead minnows and brown trout exposed at site 4 for 96 h in 1986. There was no significant difference between PCP levels in the walleye, brown trout and fathead minnows with mean values of 113 ng/g ± 12 ng/g, 215 ng/g ± 174 ng/g and 117 ng/g ± 159 ng/g, respectively.

For 2,4,6 - TCP, brown trout levels (139 ng/g ± 30 ng/g) were significantly less ($p > 0.05$) than those in the walleye (200 ng/g ± 0, N = 3), while there was no significant difference between the walleye and fathead minnow (440 ng/g ± 311) results. The differences that were found in these comparisons can be accounted for on a

Table 16: A Comparison of Chlorophenol Bioaccumulation by Fathead Minnows in 1985 vs. 1986

Site		1985 RESULTS				1986 RESULTS			
				Chlorophenol Residues (ng/g)				Chlorophenol Residues (ng/g)	
No.	Description	No. of Composite Samples	% Fat Content	2,4,6-Tri-chlorophenol	Penta-chlorophenol	No. of Composite Samples	% Fat Content	2,4,6-Tri-chlorophenol	Penta-chlorophenol
-	Pre-exposure Fish from Lab.	5	7.2±1.2	nd	nd	-	-	-	-
C 1	Control-upstream of Hwy #61A	5	5.7±1.0	nd	nd	4	7.0±0.6	nd	nd
2	Downstream of Diffuser-30m - central site	5	7.3±1.4	766±301	61±25[1]	4	-	846±831	404±343
4	Downstream of "Red Intake" - 30m	5	6.1±0.8	247±179	39±19[1]	3	-	440±312	117±160
6	Offshore of "Clean Water" Discharge	4	6.8±0.4	125±45	nd	4	-	150±28	54±58

Note: [1] In certain cases, mean values were obtained from data in which some data points were less than the detection level of 50 ng/g and in those cases an arbitrary value of ½ the detection level was assigned (i.e., 25 ng/g) in order to calculate that mean.

Table 17

Chlorophenol residues in composite samples of young-of-the-year Walleye caught in the vicinity of study site 5 during the week of August 11th, 1986.

Composite	Fat	Chlorophenol Residues (ng/g)	
		2,4,6-Trichlorophenol	Pentachlorophenol
1	NA	200	120
2	NA	200	100
3	NA	200	120
$\bar{x}$		200	113
S.D.		0	±11.6

NA - denotes not available

NOTE - mean of individual fish weights was 4.8g ± 0.9
mean of individual fish lengths (total) was 88mm ± .08mm.

- of the chlorophenols listed below, only the ones presented in the table were detected.

Chlorophenol Analyses Undertaken		Detection Levels (ng/g)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,4,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5,6-Tetrachlorophenol	(2,3,5,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

between species basis, based on the results from the in situ portion of this study. (ie. fathead minnow versus brown trout or smallmouth bass data).

Therefore, these results demontrate that bioconcentration of chlorophenols in caged fish is representative of results for indigenous fish.

3. Significance of Chlorophenols in the Kam River

Concentrations of PCP potentially lethal to fish were measured in the Kam River during this study (214,000 ng PCP/L, site 6, study day 1, 1985). No lethality was produced during that time, due to a limited exposure period of less than 24h. However, PCP levels were above the USEPA criteria for a one hour exposure period, which should not be exceeded more than once every three years. In this study, the criteria at site 6 on day 1 would have been 10,000 ng/L based on the USEPA criteria formula of

$$[PCP] = e^{[1.005\ (pH)\ -\ 4.830]}\text{, in }\mu g/L,$$

where in this case the pH was 7.1 (USEPA, 1986). The MOE criteria of <500 ng PCP/L was met in all but two cases during the 1985 study and all cases in 1986.

A survey undertaken by MNR and Lakehead University demonstrated that much of the river below the mill was devoid of or greatly underutilized by fish stocks during certain times of the summer, and fish movements in and out of the lower Kam River and into Thunder Bay harbour were dependant on oxygen levels in the river (Momot, unpub. report). If oxygen is removed as a limiting factor in regard to the presence of fish, the full potential of the Kam River as a salmon rearing site could be realized. The lower Kam River offers a holding capacity for fish, much greater than in the middle or upper river. It would be an excellent pre-smolt nursing area, very necessary for young fish growth (Momot, unpub. report).

PCP can stimulate or reduce fish growth (Cleveland, 1982) by increasing appetite and feeding, or reducing food conversion efficiency (Borgmann and Ralph, 1986). The outcome in the balance can be tipped either way although the literature has more evidence of growth inhibition. Cleveland (1982) found that Dowicide EC-7 (91% PCP) stimulated growth, while purified PCP (99%) and an industrial PCP composite decreased growth. The lowest PCP concentration at which Cleveland found fish growth reduction was 13,000 ng/L. That value is well above levels found in the Kam river on a daily basis. Matida (1976) observed a 27% growth inhibition in fish over a 28-day period at 7400 ng PCP/L, while Webb and Brett (1973) found food conversion in sockeye salmon (Oncorhynchus nerka) to be impaired at 1800 ng NaPCP/L and growth reduced at a 1,740 ng NaPCP/L concentration over a 56-day period. Under normal mill operating conditions during this study, PCP levels ranged from non detectable to 130 ng/L in the river. These levels are less than 1/10 of the lowest PCP levels known to produce sub-lethal effects on fish, and therefore pose no direct concern in regard to a potential fishery in the lower Kam River.

Research has also been undertaken to evaluate the effects of PCP body burdens in fish on fish-eating wildlife. PCP levels of greater than 2.0 µg/g (ppm) in fish would be required to produce 1 cancer in 100 fish-eating birds

(Newell et al. 1987). This level is 5 times greater than the highest values found in this study.

Chlorophenols are accumulated mainly in the liver or gall bladder of the fish, with decreasing amounts in the rest of the fish as follows: blood, kidney, spleen, skin and bone, gills, gonads and muscle (flesh) respectively (McKim et al, 1986; Glickman et al, 1977). Vaillancourt (pers. comm.) reports that detectable levels (>50 ng/g) have never been found in fish fillets analyzed for the OME Sport Fish Program. Therefore PCP in fish is not a concern in regard to human health.

In regard to 2,4,6-TCP exposures, sites 1,2 & 7 had at least two water samples greater than 1,000 ng TCP/L, approximately 10 times higher than the highest PCP level in this study. The 2,4,6-TCP isomer is considered to be an animal carcinogen by the NCRI (USEPA, 1980), however an evaluation of the effect of this CP on aquatic biota or their consumers is not possible due to the lack of research in the aquatic environment. As is the case with PCP, the lack of detectable 2,4,6-TCP levels in the flesh of sport fish in any area of Ontario including Thunder Bay (Vaillancourt, pers. comm.), addresses any concern in this regard.

CONCLUSIONS

1. During the 1985 and 1986 studies, the Great Lakes Forest Products' Diffuser effluent did not meet the fish survival requirement of the Ontario Government. The average 96-h LC50s in laboratory bioassays were 42.3% and 29.7% in the 1985 and 1986 studies, respectively.

2. The Great Lakes Forest Products' Diffuser effluent produced mortality in caged fish in two main sections of the river downstream of the mill. Those sections of river extended from 30 m downstream of the Diffuser to the inflow to the Westfort Turning Basin and from the Hwy 61B swing bridge downstream into the Mission River to at least as far as the Hydro property.

3. The Great Lakes Forest Products' mill effluent, in combination with low-flow river conditions, has produced fish kills in the Kam River at various times since 1966, and continues to have the potential to produce acutely lethal conditions for fish under current effluent treatment conditions.

4. The primary cause of acute lethality downstream of Great Lakes Forest Products was depressed dissolved oxygen (DO) levels present in the river, with critical exposure levels occurring at or below 3.0 mg DO/L over periods of 24 h. Fish mortality may also occur at DO levels in excess of 3.0 mg/L when exposure times exceed 24h.

5. The capacity of the river to assimilate the BOD demands of the waste is inadequate when the plant is running at full capacity and there are low flow conditions in the river.

6. Under certain mill operating conditions, spring and summer water temperatures and low flow river conditions, the Kam River downstream of Hwy. #61A would be unsuitable as a pre-smolt nursing area for hatchery-reared salmon.

7. Under certain mill operating conditions, spring and summer water temperatures and low flow river conditions, a zone of passage for fish migrations or movements may not exist in part of the lower Kam River, due to the effects of the GLFP's mill effluent on dissolved oxygen levels in the river.

8. The bioaccumulation of chlorophenols by indigenous and caged fish occurred in the Kam River downstream of the GLFP pulp and paper mill, and levels in the caged fish were fairly indicative of those in young-of-the-year walleye collected from the river during the fish caging study.

9. During a discharge of high chlorophenol levels such as occurred once during the 1985 study, a detrimental effect on the fishery could occur within a small localized zone of the river adjacent to the mill outfalls. However, on a day-to-day basis, chlorophenol levels in the river met the Provincial Water Quality Objectives for the protection of aquatic life.

10. Under normal mill operating conditions, chlorophenol bioaccumulation by fish would not likely have a detrimental effect on the fishery, nor be a concern in regard to the human consumption of resident fish.

RECOMMENDATIONS

1. Great Lakes Forest Products should reduce levels of oxygen demanding components in its pulp mill effluent in order to comply with the minimum dissolved oxygen requirements of the Ministry's Water Quality Guidelines, under worst case river conditions.

2. Great Lakes Forest Products should ensure that chlorophenols are discharged from the plant in such a way as not to impair the quality of fish adjacent to effluent discharges of the plant.

3. Great Lakes Forest Products should reduce the toxicity of their final effluent in order to meet or exceed the ~~federal~~ provincial government's toxicity requirement for fish.

4. A fish survey should be undertaken in the Kam River downstream of Great Lakes Forest Products to document improvements in utilization of the river by fish after reductions of BOD loadings to the river have been achieved by the mill. The fish survey of the Kam River carried out in the summer of 1987 as part of the Thunder Bay Harbour Remedial Act Plan program would provide an excellent pre-treatment evaluation for such a study.

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Appendix 1

Laboratory bioassay results for the Great Lakes Forest Products total mill effluent[1] during the August 1985 and 1986 surveys (Study Days 1-5, respectively)

			Fish Mortality/Test Solution		
Sample Type	Sample Day/Date	Bioassay[2] LC50 (%v/v)	Effluent Concentration (%v/v)[4]	Fish Mortality (%)	LT20(h)[3] for 65% Effluent
grab	1/12/8/85	45.5	100	100	26
		(65,32)[5]	65	100	
			32	0	
grab	4/15/8/85	51	100	100	36
		(59,44)	65	80	
			32	0	
grab	5/15/8/86	35.5	100	100	20
		(44,29)	65	100	
			32	30	
			18	10	
			10	0	

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1) Total mill effluent is a sample of diffuser and "clean" water effluent mixed together in proportion to their discharge flows to the Kam River, and is considered by the OME NW region as representative of the mill sample to be tested using the federal fish toxicity criteria.

2) Results calculated using the Spearman-Karber Method or Binomial Test Method

3) LT20 - time required to produce 20% fish lethality in the 65% effluent, the acute lethality limit set in the federal regulations for pulp and paper effluent (i.e. represents the test time at which the federal fish toxicity criteria was exceeded).

4) % v/v represents: volume of effluent/total test volume, expressed as a percentage.

5) Upper and lower 95% confidence levels, respectively.

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Appendix 2

Raw data for Chlorophenol residues in Fathead Minnows and Smallmouth Bass caged in the Kam River up and downstream of the GLFP's effluent diffuser during the period from August 12-16, 1985

1. Fathead Minnow Data

Site		Residue in						
		Chlorophenol	Sample #					
No.	Description	Species	1	2	3	4	5	$\bar{x}$±SD
-	Pre-exposure Fish from Lab.	All	nd	nd	nd	nd	nd	-
C-1	Control-upstream of Hwy #61A	All	nd	nd	nd	nd	nd	-
1	Downstream of Diffuser-60m - far shore site	PCP	<50	<50	60	60	65	47±20
2	Downstream of Diffuser-30m - central site	2,4,6-TCP	600	940	1200	640	450	766±301
3	Downstream of Diffuser-60m - nearshore site	2,4,6-TCP	350	520	270	450	240	366±119
		2,3,4,6-TTCP	<50	<50	<50	<50	50	-
		PCP	50	<50	<50	<50	50	35±14
4	Downstream of "Red" Intake - 30m	2,4,6-TCP	190	200	310	510	<50	247±179
		PCP	<50	60	<50	60	<50	39±19
5	Turning Basin Inflow	2,4,6-TCP	180	240	140	170	-	183±42
6	Offshore of "Clean Water" Discharge	2,4,6-TCP	130	150	160	60	-	125±45
7	Turning Basin Outflow - southern shoreline	2,4,6-TCP	<50	<50	110	160	<50	69±63
8	Hwy 61B Swing Bridge	2,4,6-TCP	115	120	60	65	<50	77±40
		PCP	<50	<50	<50	<50	75	-
9	Upstream of Mission River - 300m - south shoreline	2,4,6-TCP	<50	70	<50	105	<50	50±36

... Continued

2. Smallmouth Bass

Site		Residue in						
No.	Description	Chlorophenol Species	Sample # 1	2	3	4	5	x̄±SD
-	Pre-exposure Fish from Lab.	All	nd	nd	nd	nd	nd	-
C-1	Control - upstream of Hwy #61	All	nd	nd	nd	nd	nd	-
2	Downstream of Diffuser-30m - central site	2,4,6-TCP	50	<50	<50	230	170	100±94
		PCP	60	<50	<50	60	60	46±19
4	Downstream of "Red Intake" - 30m	2,4,6-TCP	165	165	160	155	170	163±6
		PCP	60	50	50	50	50	52±5

Note: (i) <50, <100 or nd indicates below the level of detection

(ii) all samples were analyzed for the chlorophenols listed below. Data is presented in the table only for those samples in which detectable levels were found.

Chlorophenol Analyses Undertaken		Detection Levels (ng/g)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,4,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,4 6-Tetrachlorophenol	(2,3,5,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

Appendix 3

Raw data for chlorophenol residues in Brown Trout and Fathead Minnows caged in the Kam River up and downstream of the GLFP's effluent diffuser during the period from August 11-15, 1986

1. Brown Trout

Site		Residue in						
					Sample #			
No.	Description	Chlorophenol Species	1	2	3	4	5	x±SD
-	Pre-exposure Fish from Lab.	All	nd	nd	nd	nd	nd	-
C-1	Control-upstream of Hwy #61A	All	nd	nd	nd	nd	nd	-
1	Downstream of Diffuser-60m - far shore site	2,4,6-TCP	170	-	-	-	-	-
2*	Downstream of Diffuser-30m - central site	2,4,6-TCP	140	80	110	-	-	110±30
		PCP	<50	110	130	-	-	88±56
3	Downstream of Diffuser-60m - nearshore site	2,4,6-TCP	120	140	110	120	80	114±22
		PCP	<50	160	160	140	90	115±58
4	Downstream of "Red" Intake - 30m	2,4,6-TCP	125	110	180	140	-	139±30
		PCP	305	120	410	<50	-	215±174
5	Turning Basin Inflow	2,4,6-TCP	140	<50	170	70	-	101±66
6	Offshore of Clear Water Discharge	2,4,6-TCP	180	180	90	80	100	126±50
		PCP	<50	<50	110	80	120	72±45
7	Turning Basin Outflow - southern shoreline	2,4,6-TCP	120	60	160	140	190	134±49
		PCP	150	80	210	100	190	146±56
8	Hwy 61B Swing Bridge - mid river	2,4,6-TCP	180	120	190	190	-	170±34
		PCP	500	140	250	130	-	255±172
9	300m Upstream of Mission - River - south shoreline	2,4,6-TCP	110	90	250	200	160	162±65
		PCP	50	90	250	160	90	128±79

... Continued

Appendix 3
(Continued)

Site		Residue in						
No.	Description	Chlorophenol Species	1	2	Sample # 3	4	5	x±SD
10	Mission River - 900m downstream of connection to the Kam River	2,4,6-TCP	330	220	160	110	690	302±232
		PCP	340	520	70	70	410	282±204
11*	Mission River - 400m downstream of Marina - east shoreline	2,4,6-TCP	420	440	630	-	-	497±116
		PCP	290	570	240	-	-	367±178

2. Fathead Minnows

Site		Residue in						
No.	Description	Chlorophenol Species	1	2	Sample # 3	4	5	x± SD
-	Pre-exposure Fish from Lab.	-	-	-	-	-	-	-
C-1	Control - upstream of Hwy #61	All	nd	nd	nd	nd	-	-
2	Downstream of Diffuser-30m - central site	2,4,6-TCP	290	1270	1800	<50	-	846±831
		PCP	240	540	810	<50	-	404±343
4	Downstream of "Red Intake" - 30m	2,4,6-TCP	800	260	260	-	-	440±312
		PCP	300	<50	<50	-	-	117±159
6	Offshore of "Clean Water" Discharge - 30m	2,4,6-TCP	170	170	110	150	-	150±28
		PCP	<50	<50	140	<50	-	54±58

Note: (i) <50, <100 or nd indicates below the level of detection

(ii) * - analyses undertaken on fish which died during the exposure

Chlorophenol Analyses Undertaken		Detection Levels (ng/g)
2,3,4-Trichlorophenol	(2,3,4 TCP)	100
2,4,5-Trichlorophenol	(2,4,5 TCP)	50
2,4,6-Trichlorophenol	(2,4,6 TCP)	50
2,3,4,5-Tetrachlorophenol	(2,3,4,5 TTCP)	50
2,3,5 6-Tetrachlorophenol	(2,3,4,6 TTCP)	50
Pentachlorophenol	(Penta CP)	50

Appendix 4

Conductivity levels (umhos/cm) and calculated Mill Effluent concentrations (%) at sites in the Kam River where acute lethality was observed immediately downstream of Great Lakes Forest Products' diffuser discharge August 12 - 16, 1985 (study days 1 - 5)

Site		Conductivity & Related Effluent Concentrations (in brackets)[1] on Study Days				
No.	Description	1	2	3	4	5
1	Downstream of Diffuser-60m - far shore site	184 (8%)	171 (5%)	226 (7%)	259 (8%)	-
2	Downstream of Diffuser-30m - central site	189 (8%)	198 (7%)	253 (9%)	259 (8%)	-
3	Downstream of Diffuser-60m - nearshore site	174 (7%)	-	194 (5%)	218 (6%)	-
4	Downstream of "Red" Intake - 30m	154 (5%)	95 (1%)	259 (10%)	216 (6%)	-
5	Turning Basin Inflow	173 (7%)	140 (3%)	197 (5%)	190 (4%)	-
	Other Pertinent Sites					
	Control - at GLFP's Water Intake	84	91	125	124	
	Diffuser Effluent (Full Strength)	1390	1670	1490	1750	

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[1] Effluent Concentrations based on Relative Conductivity (C_R) using test Formula $C_R = \frac{C_ts - C_c}{C_e - C_c}$, where C_ts = conductivity at a specific test site.

C_c = conductivity at a river control site,

and C_e = conductivity of the full strength effluent sample.

Note: All values obtained from grab samples.

APPENDICES 5 & 6

Appendix 5

Resin Acid concentrations (µg/L) in the Great Lakes Forest Products Diffuser effluent during the period from August 12-16, 1985 (study days 1-5)

Resin Acids	Concentrations (µg/L) at Study Sites			
	Days 1-2	2-3	3-4	4-5
Palustric	nd	nd	nd	nd
Pimaric	10	10	10	10
Sandaracopimaric	180	125	135	145
Levopimaric	200	130	135	160
Isopimaric	200	130	135	160
Neoabietic	270	125	85	200
Abietic	4130	2670	2735	2465
Dehydroabietic	1130	760	770	840
m-Chlorodehydroabietic	200	85	85	48
Dichlorodehydroabietic	nd	nd	nd	nd

Appendix 6

Resin Acid concentrations (µg/L) in the Great Lakes Forest Products Diffuser effluent during the period from August 12-16, 1985 (study days 1-5)

Resin Acids	Concentrations (µg/L) at Study Sites				
	Days 1	2	3	4	5
Palustric	-	-	-	-	-
Pimaric	21	16	10	11	nd
Sandaracopimaric	27	20	11	13	nd
Levopimaric	98	45	30	42	nd
Isopimaric	72	40	36	29	nd
Neoabietic	50	18	30	18	nd
Abietic	650	350	270	240	nd
Dehydroabietic	<10	<10	180	140	nd
m-Chlorodehydroabietic	85	46	nd	nd	nd
Dichlorodehydroabietic	nd	nd	nd	nd	nd

nd - not detected
Detection Level - 10 µg/L for all of the listed compounds
Analyses were undertaken on 24-h composite samples collected from noon until noon on the study days denoted above.

Appendix 7

Organosulfur compound concentrations in daily grab samples of GLFP's effluents collected August 11-15, 1986 (Study Days 1-5, respectively)

1. DIFFUSER EFFLUENT

Organosulfur Species	Concentrations (ug/L) on Study Days				
	1	2	3	4	5
Carbonyl Sulfide	nd	nd	nd	nd	0.30
Carbon Disulfide	0.40	0.40	0.90	0.30	0.50
Dimethyl Sulfide	0.30	0.30	0.90	nd	nd
Hydrogen Sulfide	0.70	0.60	nd	nd	3.90
Sulfur Dioxide	nd	nd	nd	nd	0.30
Totals	1.40	1.30	1.80	0.30	5.00

2. CLEAN WATER EFFLUENT DISCHARGE

No organosulfur compounds detected.

Note:

(1) test results are considered as minimum values
(2) detection level for all sulfides: 0.30 µg/L
(3) nd - not detected
(4) the test method does not differentiate between carbonyl sulfide and sulfur dioxide
(5) the samples were also analyzed for: dimethyl disulfide ethyl mercaptan, methyl mercaptan and thiophene, but were not detected at levels above 0.30 µg/L

Appendix 8

Phenoxy Acid concentrations (ng/L) in the Kam River up and downstream of the Great Lakes Forest Products diffuser on August 11 - 15/86 (Study Days 1 - 5 respectively)

STUDY DAY/ Phenoxy Acid Species	Concentrations (ng/L) at Study Sites												
	C-1	C-2	1	2	3	4	5	6	7	8	9	10	11
DAY 1													
2,4 - DP	nd	nd	nd	nd	nd	550	610	nd	nd	nd	nd	nd	nd
2,4 - DB	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	310'	nd
DAY 2													
2,4 - DP	nd	nd	-	-	nd	720	nd	nd	nd	nd	nd	nd	nd
DAY 3	No phenoxy acids detected												
DAY 4	No phenoxy acids detected												
DAY 5	No phenoxy acids detected												

Phenoxy Acid Analyses Undertaken	Detection Levels (ng/L)
Dicamba	100
2,4 - Dichlorophenoxypropionic Acid (2,4 DP)	100
2,4 - Dichlorophenoxyacetic Acid (2,4 D)	100
Silvex	50
2,4,5 - Trichlorphenoxyacetic Acid (2,4,5 T)	50
2,4 - Dichlorophenoxybutyric Acid (2,4 DB)	200

Note:

nd - not detected
- - sample not analyzed
' - phenoxy acid concentrations <500 ng/L are tentative and are provided as information only.

Appendix 9

Conductivity (µmhos/cm) in the Kam River up and downstream of the Great Lakes Forest Products diffuser during the period from August 12-16, 1985 (Study Days 1, 2, 3, and 4)

Conductivity (@25°C) on Day #	Diffuser Effluent	C-1	C-2	Concentrations at Study Sites								
				1	2	3	4	5	6	7	8	9
1	1390	84	84	184	189	174	154	173	247	142	-	-
2	1670	90	91	171	198	-	95	140	195	180	182	158
3	1490	121	125	226	253	194	259	197	263	180	180	162
4	1750	126	124	259	259	218	216	190	238	216	201	187

Appendix 10

Conductivity (µmhos/cm) in the Kam River up and downstream of the Great Lakes Forest Products Diffuser during the period from August 11-15, 1986 (Study Days 1-5)

Conductivity (@25°C) on Day #	Diffuser Effluent	C-1	Concentrations at Study Sites										
			1	2	3	4	5	6	7	8	9	10	11
1	2150	90	275	255	-	250	205	250	195	195	165	150	140
2	1750	95	290	273	195	240	125	275	275	215	200	170	145
3	1450	85	310	235	260	255	235	300	270	250	220	225	185
4	1350	75	220	305	200	165	195	230	240	220	200	290	240
5	2000	85	310	300	135	310	210	260	260	260	-	-	-

Note: These appendices contain the raw data used in Table 10 and Appendix 4.

Appendix 11

Dissolved Oxygen (mg/L) and Temperature (°C) in the Kam River up and downstream of the Great Lakes Forest Products diffuser during the period from August 12-16, 1985 (Study Days 1-5)

Dissolved Oxygen (mg/L) on Day #	Values at Study Sites										
	C-1	C-2	1	2	3	4	5	6	7	8	9
1	8.6	8.3	8.0	7.6	7.6	7.6	7.6	5.9	6.5	6.0	5.7
2	8.3	8.2	–	8.3	–	7.0	7.9	6.3	5.7	5.4	4.8
3	8.5	8.3	8.0	8.0	8.0	7.8	8.0	5.7	5.8	5.4	5.0
4	8.8	8.6	8.3	8.3	8.3	8.4	8.2	6.4	6.7	6.0	4.9
5	8.8	8.5	8.2	8.2	8.2	8.3	8.1	6.9	7.6	7.2	5.2

Appendix 12

Dissolved Oxygen (mg/L) in the Kam River up and downstream of the Great Lakes Forest Products Diffuser during the period from August 11-15, 1986 (Study Days 1-5)

Dissolved Oxygen (mg/L) on Day #	Values at Study Sites											
	C-1	1	2	3	4	5	6	7	8	9	10	11
1	7.2	7.8	7.3	7.5	7.2	7.3	5.2	7.2	6.0	3.8	3.6	4.5
2	8.8	8.3	8.9	8.6	9.0	8.1	4.1	4.2	3.4	2.4	3.1	4.3
3	8.0	8.0	7.8	7.6	7.8	7.9	3.4	5.0	3.6	0.5	0.8	2.7
4	8.6	8.0	7.6 (6.9)*	8.3	8.5 (8.0)	8.2	5.0	4.8	2.6	–	–	1.6
5	8.3	7.5	7.9 (5.9)	8.0 (7.8)	7.0 (6.8)	7.6	3.8	4.7	3.8	–	–	–

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*Values in brackets represent dissolved oxygen levels measured in the cages.

Appendix 13

pH Levels in the Kam River up and downstream of the Great Lakes Forest Products diffuser during the period from August 12-15, 1985 (Study Days 1 - 4, respectively)

pH on Day #	Diffuser Effluent	C-1	C-2	1	2	3	4	5	6	7	8	9
1	6.8	7.7	7.7	7.1	7.1	7.1	7.1	7.0	7.1	7.2	7.2	7.2
2	6.1	7.8	7.7	7.2	7.1	-	7.7	7.1	7.2	7.2	7.2	7.3
3	5.9	7.8	7.8	7.0	6.9	7.1	7.0	7.1	7.1	7.3	7.2	7.1
4	6.1	7.9	7.9	7.3	7.4	7.4	7.4	7.5	7.4	7.4	7.3	7.3

Appendix 14

pH Levels in the Kam River up and downstream of the Great Lakes Forest Products diffuser during the period from August 11-15, 1986 (Study Days 1-5 respectively)

pH on Day #	Diffuser Effluent	C-1	1	2	3	4	5	6	7	8	9	10	11
1	7.4	8.0	7.3	7.3	7.9	7.3	7.3	7.2	7.3	7.2	7.2	7.1	7.2
2	6.2	8.0	7.2	7.2	7.3	7.2	7.4	7.0	7.0	7.0	7.1	7.0	7.1
3	7.2	8.0	7.3	7.4	7.3	7.3	7.3	7.1	7.2	7.2	7.1	7.2	7.4
4	6.6	7.7	7.3	7.2	7.4	7.4	7.3	7.2	7.2	7.2	-	-	7.1
5	6.7	7.6	7.2	7.2	7.4	7.0	7.3	6.8	7.1	7.0	-	-	-